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# NUCLEAR MAGNETIC RESONANCE

## TECHNICAL REPORT No. VI

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### CONTENTS

1. **Electron Distribution in Molecules. I.  $F^{19}$  Nuclear Magnetic Shielding and Substituent Effects in Some Benzene Derivatives;** H. S. GUTOWSKY, D. W. MCCALL, B. R. MCGARVEY, and L. H. MEYER; Reprinted from the Journal of the American Chemical Society, **74**, 4809-4817 (1952).
2. **Nuclear Magnetic Resonance in Metals. I. Broadening of Absorption Lines by Spin-Lattice Interactions;** H. S. GUTOWSKY and B. R. MCGARVEY; Reprinted from the Journal of Chemical Physics, **20**, 1472-1477 (1952).
3. **Nuclear Magnetic Resonance Multiplets in Liquids;** H. S. GUTOWSKY, D. W. MCCALL, and C. P. SLICHTER; Reprinted from the Journal of Chemical Physics, **21**, 279-292 (1953).
4. **Electron Distribution in Molecules. II. Proton and Fluorine Magnetic Resonance Shifts in the Halomethanes;** L. H. MEYER and H. S. GUTOWSKY; Reprinted from the Journal of Physical Chemistry, **57**, 481-486 (1953).
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## Electron Distribution in Molecules. I. $F^{19}$ Nuclear Magnetic Shielding and Substituent Effects in Some Benzene Derivatives<sup>1</sup>

BY H. S. GUTOWSKY, D. W. MCCALL, B. R. MCGARVEY AND L. H. MEYER

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The influence of substituents on the electron distribution in benzene produces changes in the nuclear magnetic shielding of fluorine atoms in the molecule. A comparison of the  $F^{19}$  nuclear magnetic shielding in fluorobenzene with that in a substituted fluorobenzene is used in defining a  $\delta$ -parameter. Experimental  $\delta$ -values are reported for a considerable number of mono- and polysubstituted fluorobenzenes. An empirical correlation of  $\delta$ -values for meta and para substituents with the corresponding Hammett substituent  $\sigma$ -constants reveals systematic differences which are attributed to the dependence of the  $\delta$ -values on the nature of the electronic interactions of the substituent. Thereby, a detailed analysis of the  $\delta$ - and  $\sigma$ -values for particular substituents permits evaluation of the nature of their electronic effects. Consideration of ortho substituents suggests that besides the usual inductive and electromeric effects at the meta and para positions, an additional interaction contributes to the  $\delta$ -values in some cases. The potential uses and limitations of  $\delta$ -values in evaluating ortho-effects and entropies of reaction are discussed. It is concluded from  $\delta$ -values for polysubstituted fluorobenzenes that the electronic effects of substituents are usually remarkably additive but with significant non-additivity demonstrating interactions between substituents in about a third of the compounds investigated. A  $\delta'$ -parameter, analogous to  $\delta$ , is defined in terms of the change produced by a substituent in the ring on the  $F^{19}$  nuclear magnetic shielding in benzotrifluorides. The  $\delta'$ -values are about a tenth of the  $\delta$ -values for the same substituent, indicating the extent of attenuation in the side chain of the substituent effects. Less conclusive discussions and comparisons are given of various other aspects of the data and experimental method.

### Introduction

Several features of the microwave and radio-frequency spectra of molecules are associated with their electronic structure. Nuclear electric quadrupole splittings of microwave rotational spectra<sup>2a</sup> and the radiofrequency pure quadrupole spectra<sup>2b,c</sup> are determined by the variation in electrostatic field at the nucleus. Electric field gradients have been calculated for assumed electronic structures and compared with experimental values to give considerable information about bond hybridization.<sup>2a</sup> This report is concerned primarily with another similar effect, the magnetic shielding of fluorine nuclei<sup>3</sup> and its dependence upon substituents in fluorobenzenes.

Nuclei with magnetic moments exhibit radio-frequency spectra in the one to forty megacycle range when placed in magnetic fields of 5,000 to 10,000 gauss.<sup>4</sup> Resonance absorption, corresponding to the reorientation of the nuclear magnetic moment with respect to the applied magnetic field direction,<sup>5</sup> occurs at a frequency given by the Larmor equation,  $\nu = g\beta H_0/h$ .  $g$  is the nuclear gyromagnetic ratio,  $\beta$  is the nuclear magneton and  $H_0$  is the magnetic field at the nucleus. However, the magnetic field at a nucleus differs to a small but measurable extent from the magnetic field in the macroscopic sample.<sup>6</sup> The applied magnetic field interacts with the motions of the electrons in the system, which thereby contribute a component to the net magnetic field at the nucleus. This electronic component is proportional to the

applied field and is usually in the opposite direction. The effect may be considered an internal diamagnetism or a magnetic shielding of the nucleus.

The magnitude of this nuclear magnetic shielding depends upon the nucleus and the electronic structure of the sample in which it is observed.<sup>7</sup> A general theory has been proposed<sup>8</sup> for nuclear magnetic shielding in molecules, but the complexity of the calculations has restricted application thus far to the hydrogen molecule. However, in an experimental survey of the binary covalent fluorides, the  $F^{19}$  magnetic shielding was found<sup>9</sup> to decrease approximately linearly with increasing electronegativity of the atom to which the fluorine is bonded. A reasonably accurate physical picture is that the more tightly electrons are held by the atom bound to the fluorine, the less effective they are in shielding the fluorine. These empirical results suggested that  $F^{19}$  magnetic shielding values might serve to evaluate electronegativities, or electron densities. At least, the fluorine magnetic shielding in a molecule is related directly to the electron distribution of the group bound to the fluorine.

Some preliminary measurements have been reported<sup>9</sup> for an  $F^{19}$  shielding parameter,  $\delta$ , defined in terms of the change in shielding caused by a substituent in fluorobenzene. Substituents in benzene of course influence a considerable variety of other properties.<sup>10-12</sup> In most instances it is generally

(1) Supported in part by ONR.

(2) (a) C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949); (b) H. G. Dehmelt and H. Krüger, *Naturwissenschaften*, **37**, 111 (1950); (c) R. Livingston, *Phys. Rev.*, **83**, 289 (1951).

(3) H. S. Gutowsky and C. J. Hoffman, *J. Chem. Phys.*, **19**, 1259 (1951), and references cited therein.

(4) (a) E. M. Purcell, H. C. Torrey and R. V. Pound, *Phys. Rev.*, **69**, 37 (1946); (b) F. Bloch, W. W. Hansen and M. Packard, *ibid.*, **69**, 127 (1946).

(5) (a) E. M. Purcell, *Science*, **107**, 433 (1948), gives an excellent introductory description of nuclear magnetism; (b) G. E. Pake, *Am. J. Phys.*, **18**, 438, 473 (1950), has published a more detailed discussion and a bibliography.

(6) (a) W. E. Lamb, Jr., *Phys. Rev.*, **60**, 817 (1941); (b) W. C. Dickinson, *ibid.*, **60**, 563 (1950).

(7) (a) W. D. Knight, *ibid.*, **76**, 1259 (1949); (b) W. G. Proctor and F. C. Yu, *ibid.*, **77**, 717 (1950); (c) W. C. Dickinson, *ibid.*, **77**, 736 (1950).

(8) N. F. Ramsey, *ibid.*, **78**, 609 (1950).

(9) (a) H. S. Gutowsky, D. W. McCall, B. R. McGarvey and L. H. Meyer, *J. Chem. Phys.*, **19**, 1328 (1951); (b) an earlier suggestion was given by H. S. Gutowsky and C. J. Hoffman, *Phys. Rev.*, **80**, 110 (1950).

(10) (a) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 183; (b) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford at the Clarendon Press, London, 1949, pp. 50, 160; (c) L. P. Hammett, "Physical Organic Chemistry," 1st Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

(11) C. K. Ingold, *Chem. Revs.*, **15**, 225 (1934).

(12) (a) L. E. Sutton, *Proc. Roy. Soc. (London)*, **133A**, 668 (1931); (b) L. E. Sutton, *Trans. Faraday Soc.*, **30**, 789 (1934).

agreed that the effects result primarily from the perturbing influence of the substituent on the molecular electronic distribution. Among the properties affected are reactivities and orientation in substitution reactions,<sup>11</sup> dipole moments,<sup>12</sup> the dissociation constants<sup>13</sup> or relative rates of reaction<sup>10c</sup> of substituted compared to unsubstituted compounds, spectroscopic moments<sup>14</sup> and vibrational frequencies.<sup>15</sup> A comparison of the Hammett substituent constants,<sup>10c</sup>  $\sigma$ , with the corresponding preliminary  $\delta$ -values revealed<sup>9a</sup> a fairly linear correlation. In this article are presented the experimental details,  $\delta$  values for a wide variety of monosubstituted and polysubstituted fluorobenzenes, and similar data for several benzotrifluorides. A detailed comparison of  $\sigma$  and some of the other substituent effects with the considerable number of  $\delta$ -values now available confirms their general similarity, and develops several interesting exceptions.

### Experimental

**Apparatus and Procedure.**—Figure 1 is a block diagram of the experimental arrangement. The spectroscope used a radiofrequency bridge<sup>16</sup> and was identical with that described in detail elsewhere,<sup>9</sup> except for the manner of field modulation and sample comparison. The signal generator was set at a fixed frequency of about 25.5 megacycles/second, the  $F^{19}$  magnetic resonance frequency in the 6365 gauss field of the permanent magnet. The saw-tooth voltage generated in a Dumont 304-H oscilloscope was applied at a frequency of 2 cycles/second to the horizontal axis and also to a cathode follower. The current of the latter was fed through a field modulation coil<sup>17</sup> about one magnet pole. By connecting the d.c. output of the detector in the communications receiver to the vertical axis of the oscilloscope the absorption line was displaced on the oscilloscope as a function of the magnetic field applied to the sample. In addition, the position on the oscilloscope of the absorption lines was adjustable by passing a direct current through another coil about the other pole of the magnet.

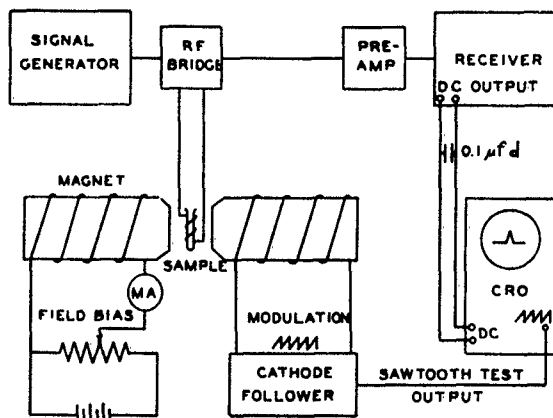


Fig. 1.—Block diagram of the radiofrequency spectroscopy with slow sweep modulation for measuring molecular differences in nuclear magnetic shielding.

Under otherwise fixed conditions, the position of an  $F^{19}$  absorption line on the oscilloscope depends upon the  $F^{19}$  mag-

netic shielding in the sample. Relative absorption intensities are proportional to the number of nuclei. Figure 2 is an oscilloscope photograph of the  $F^{19}$  absorption line in 2,3,5-trifluorobenzotrifluoride. The strong line is from the  $CF_3$  group; the three weaker lines, with equal intensities, are from the three structurally distinguishable  $F^{19}$  nuclei attached directly to the benzene ring. It is apparent that the  $F^{19}$  magnetic shielding differences are readily observable. The differences were measured quantitatively by determining the change necessary in the field biasing current to center on the oscilloscope first one resonance line and then the other. Calibration of the field biasing current in terms of magnetic field has been described.<sup>9</sup>  $\delta$ , the  $F^{19}$  magnetic shielding parameter is defined<sup>18</sup> as  $10^6 \times (H_r - H_s)/H_r$ , where  $H_r$  is the applied magnetic field for the  $F^{19}$  resonance in the given substituted fluorobenzene and  $H_r$  is that for the reference, fluorobenzene itself.

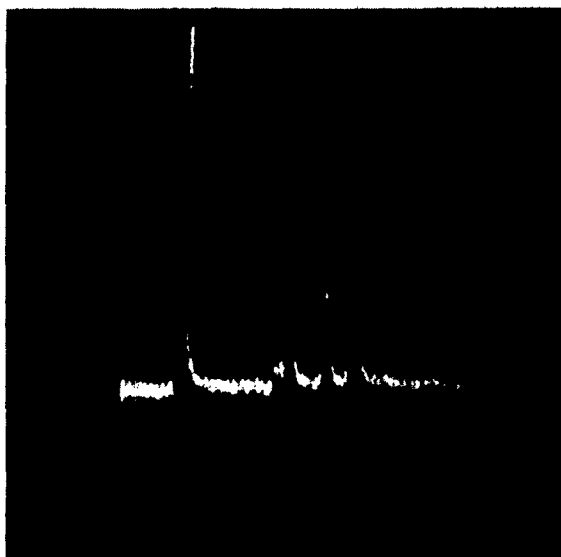


Fig. 2.—Oscilloscope photograph of the  $F^{19}$  magnetic resonance absorption lines in 2,3,5-trifluorobenzotrifluoride. The strong line is assigned to the  $F^{19}$  nuclei in the  $CF_3$  group; the three weak lines, from left to right, to the 5-, 3- and 2-fluorines. The horizontal sweep is about 0.9 gauss, increasing from left to right; total applied magnetic field, 6365 gauss.

Samples were placed in short lengths of 5-mm. o.d. Pyrex tubing, sealed at one end. These tubes fitted snugly in the r.f. coil of the bridge element in the magnetic field. Most of the samples observed were liquid at room temperature. In this event one drop was added to a drop of a reference compound and the  $F^{19}$  magnetic resonance observed on the oscilloscope. The addition of more reference compound increased the intensity of its absorption line, identifying the different lines. Fluorobenzene was used as a reference for substituted fluorobenzenes unless the separation of the absorption lines was less than about 0.007 gauss, the limiting resolution. In such cases, *p*-fluoroanisole was used as a secondary reference, and the measurements reduced to the fluorobenzene scale. For the substituted benzotrifluorides, *p*-iodofluorobenzene was used as a reference, and the values then converted to a benzotrifluoride scale, denoted as  $\delta'$ . Data on the binary covalent fluorides<sup>9</sup> have been referred to fluorine gas as an arbitrary zero.<sup>18</sup> These data were reported as relative shielding values defined as  $(H_s - H_F)/H_F$ .  $\delta$ - and  $\delta'$ -values can be converted to this scale by using the fluorobenzene and benzotrifluoride values of  $54.32 \times 10^{-6}$  and  $49.33 \times 10^{-6}$ , respectively, on the  $F_2$  scale. One should note that the signs of  $\delta$  and  $\delta'$  are reversed from that of the  $F_2$  scale.

(18) Trifluoroacetic acid is an excellent reference compound which we have used for most measurements on non-aromatic compounds, its shielding value on the  $F_2$  scale is  $50.76 \times 10^{-6}$ .

(13) J. F. J. Dippy, *Chem. Revs.*, **28**, 151 (1939).

(14) J. R. Platt, *J. Chem. Phys.*, **19**, 263 (1951).

(15) (a) M. St. C. Flett, *Trans. Faraday Soc.*, **44**, 767 (1948);

(b) A. H. Soloway and S. L. Friess, *THIS JOURNAL*, **78**, 5000 (1951).

(16) N. Bloembergen, E. M. Purcell and R. V. Pound, *Phys. Rev.*, **78**, 679 (1948).

(17) This arrangement is similar to that used earlier by J. T. Arnold, S. S. Dharmatti and M. E. Packard, *J. Chem. Phys.*, **19**, 507 (1951).

In a few cases, the samples were solid and solutions were required to obtain the narrow lines essential for accurate measurements.<sup>3</sup> Aromatic solvents, principally nitrobenzene, were used when possible because small solvent effects were found with dissimilar substances. The fluorobenzoic acids and fluoroacetanilides required ethanol to obtain a solution concentrated enough for measurement. The solutions were handled in the same manner as the liquids.

All measurements were made at room temperature.<sup>19</sup> Sources and magnitudes of errors have been discussed<sup>3</sup> for the somewhat different sample interchange and field modulation methods used earlier.<sup>3,19a</sup> The new slow sweep modulation and combined unknown-reference samples improved the consistency of these measurements. Low positive biasing currents, less than 0.5 gauss, were maintained to reduce hysteresis effects. Also, a double-pole bias switch made it possible to center the two resonances with separate rheostats. This permitted a rapid change from one resonance to another, virtually eliminating error introduced by drift in the signal generator frequency. At least one series of five to ten measurements was made on each compound, and two or three on most. The probable errors of the reported  $\delta$ - and  $\delta'$ -values are less than  $\pm 0.03$ .

**Materials.**—The compounds used were obtained from several sources. The purity was not critical as long as there was no question regarding the identity of the major constituent. In fact, observation of the  $F^{19}$  absorption lines was found quite useful on several occasions in determining the nature and extent of some fluorine-containing impurities. The *o*-fluorochlorobenzene, *p*-fluoroanisole, *p*-fluorobenzonitrile, *p*-fluorobenzenesulfonyl chloride, and 4-fluorobiphenyl were the purest grade available from Eastman Kodak Co. The *o*-fluoroanisole, and *o*-, *m*- and *p*-fluorophenoles were from Custom Chemical Co. The *p*-fluorodimethylaniline and *N*-phenyl-*p*-fluoroaniline were furnished by Dr. Nelson J. Leonard, of this department. The *o*-, *m*- and *p*-trifluoromethyl benzotrifluorides were furnished by Dr. O. R. Pierce of Purdue University. The *m*-fluorobromobenzene, *m*-fluoroiodobenzene and *m*-fluorobenzonitrile were synthesized. The remainder of the samples were supplied by Dr. Glenn C. Finger, head of the Fluorospar Division of the Illinois State Geological Survey.

## Results and Discussion

### Monosubstituted Benzene Derivatives

**A Comparison of  $\sigma$ - and  $\delta$ -Values.**—Table I lists  $\delta$ -values determined for a variety of *o*-, *m*- or *p*-monosubstituted fluorobenzenes. In Fig. 3,  $\delta$ -values from Table I are plotted against Hammett's substituent constant<sup>10c</sup>  $\sigma$  where the latter are available. It is seen that there is a general correlation between the two parameters, although scatter of individual points from a straight line is often greater than experimental error. In particular, the meta substituents follow a trend differing from that of the para substituents. A linear least squares solution for all the meta and para points gives  $\sigma = 0.600\delta + 0.243$ , with a residual sum of 2.38. Separate solutions for the meta and para points give  $\sigma_m = 1.69\delta_m$  and  $\sigma_p = 0.560\delta_p + 0.271$  with residual sums of 0.26 and 0.71, respectively.

The improvement in fitting the data by separate solutions demonstrates a fundamental difference in the particular effects operative at the meta and para positions. Of course, the general correlations between  $\sigma$ - and  $\delta$ -values confirm the accepted view that the effects of substituents on reactivity are basically electronic in nature. In addition, the previously established dependence of the  $F^{19}$  magnetic shielding on the electronegativity of the attached atom suggests that the substituent effects may be interpreted as changes in electronegativity

(19) The  $F^{19}$  shielding values appear to be temperature independent in fluorocarbons; see, e.g., reference 9b and 8

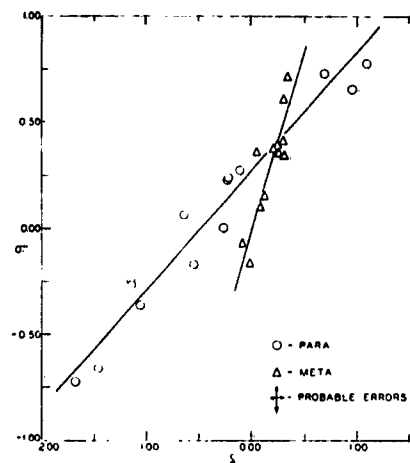


Fig. 3. A plot of Hammett's  $\sigma$  versus values of  $\delta$  from Table I, for meta and para substituents in benzene.

TABLE I

$F^{19}$  NUCLEAR MAGNETIC SHIELDING  $\delta$ -VALUES FOR MONOSUBSTITUTED BENZENE DERIVATIVES<sup>a</sup>

Substituent	Ortho $\delta$	Meta $\delta$	$\sigma$	Para $\delta$	$\sigma$
NO <sub>2</sub>	-0.56	+0.33	+0.710	+1.08	+0.778
CN	+ .52	+ .30	+ .608 <sup>d</sup>	+0.96	+ .658 <sup>d</sup>
CO <sub>2</sub> H	+ .35	+ .05	+ .355	+ .69	+ .728
I	+1.93	+ .26	+ .352	- .12	+ .276
Br	+0.55	+ .24	+ .391	- .23	+ .232
Cl	- .27	+ .21	+ .373	- .24	+ .227
F	-2.59	+ .31	+ .337	- .64	+ .062
CH <sub>3</sub>	-0.50	- .09	- .069	- .55	- .170
CH <sub>3</sub> CONH <sup>b</sup>	-1.28	+ .10	.....	- .57	.....
OH	-2.50	+ .09	+ .10 <sup>c</sup>	-1.06	- .36 <sup>c</sup>
CH <sub>3</sub> O	-2.24	.....	.....	-1.14	- .268
C <sub>2</sub> H <sub>5</sub> O	-2.17	+ .13	+ .15	-1.15	- .25
NH <sub>2</sub>	-2.31	- .02	- .161	-1.46	- .660
Substituent	$\delta$	$\sigma$	Substituent	$\delta$	$\sigma$
<i>p</i> -SO <sub>2</sub> C <sup>b</sup>	+1.26	.....	<i>p</i> -N(CH <sub>3</sub> ) <sub>2</sub>	-1.68	-0.720 <sup>f</sup>
<i>p</i> -CCl <sub>3</sub>	+0.26	.....	<i>o</i> -CH=CHCO <sub>2</sub> H <sup>c</sup>	-0.27	.....
<i>p</i> -Phenyl <sup>b</sup>	- .27	+0.009	<i>m</i> -CF <sub>3</sub>	+ .28	+ .41 <sup>g</sup>
<i>p</i> -O—C <sub>6</sub> H <sub>4</sub> —F	- .67	.....	<i>m</i> -CH(OH)CH <sub>3</sub>	.00	.....
<i>p</i> -NH—C <sub>6</sub> H <sub>4</sub> <sup>b</sup>	- .94	.....	<i>m</i> -O—C <sub>6</sub> H <sub>4</sub> —F	- .05	.....

<sup>a</sup>  $\sigma$  values are from reference 10c unless otherwise indicated.

<sup>b</sup> In ethanol solution. <sup>c</sup> In  $\text{H}-\text{C}(=\text{O})-\text{N(CH}_3)_2$  solution. <sup>d</sup> J. D. Roberts and E. A. McElhill, THIS JOURNAL, 72, 628 (1950). <sup>e</sup> Computed from the ionization constants for *m*- and *p*-hydroxybenzoic acids from reference 13. <sup>f</sup> C. C. Price and D. C. Lincoln, THIS JOURNAL, 73, 5838 (1951). <sup>g</sup> J. D. Roberts, R. L. Webb and E. A. McElhill, *ibid.*, 72, 408 (1950).

or electron density at the point of reaction. A total increase in electronegativity of 2.5 units was found<sup>3</sup> to correspond<sup>20</sup> to an increase in  $F^{19}$  magnetic shielding of  $60 \times 10^{-3}$ . The observed range of  $\delta$  in the monosubstituted benzene derivatives is 4.5, or a range in electronegativity of about 0.2, if the same relation holds. This is at best a rough estimate, particularly in view of the differences between the meta and para positions. Jaffé has computed<sup>21</sup> theoretical electron densities by molecular orbital methods for several monosub-

(20) The dependence of the  $F^{19}$  magnetic shielding on electronegativity varies somewhat for different groups in the periodic table. For all reported binary covalent fluorides  $d\delta/d\chi$  is about  $4.1 \times 10^{-3}$ , while for Group IV fluorides it is about  $6.5 \times 10^{-3}$ .

(21) H. H. Jaffé, J. Chem. Phys., 20, 778 (1952). We are indebted to Dr. Jaffé for sending us a copy of his article prior to publication.

stituted benzenes and obtained results also agreeing with the  $\sigma$ -values.<sup>22</sup>

The differences between the  $\sigma$ - and  $\delta$ -values raise some interesting questions. The line for meta substituents has a slope three times larger than that for para. Moreover, while the meta line includes the origin, the para scale is displayed systematically by +0.27. And, finally, deviations of several of the points from the appropriate meta or para curve exceed experimental error by significant amounts. Both  $\sigma$  and  $\delta$  have operational definitions so these effects must arise from factors implicit in the nature of the experiments. A possible major factor is that  $\delta$  is determined with the molecule in its normal state, while  $\sigma$  is evaluated from rate or equilibrium data and depends therefore on the character of the transition state.<sup>23</sup>

Hammett's basic definition of  $\sigma$  is

$$\sigma \equiv \log K_i - \log K_i^0 \quad (1)$$

where  $K_i$  and  $K_i^0$  are the ionization constants for the substituted and unsubstituted benzoic acids. However, a more general development is required to determine the relation of  $\sigma$  to the transition state. Accordingly, the following transition state expressions are proposed for the rate constants of the forward and reverse ionization of the substituted benzoic acid

$$k_f = \kappa \frac{kT}{h} e^{\Delta S_i^\ddagger/R} e^{-(\Delta H_i^\ddagger - \rho\sigma')/RT} \quad (2)$$

and

$$k_r = \kappa \frac{kT}{h} e^{\Delta S_r^\ddagger/R} e^{-(\Delta H_r^\ddagger + \rho\sigma')/RT} \quad (3)$$

with similar expressions, without the  $\rho\sigma'$ , for the unsubstituted benzoic acid. In the equations,  $\kappa$  is the transmission coefficient;  $k$ , Boltzmann's constant;  $h$ , Planck's constant;  $\Delta H^\ddagger$ , the enthalpy of activation exclusive of substituent effects;  $\Delta S^\ddagger$ , the entropy of activation.  $\sigma'$  is related to the substituent effect on electron distribution and  $\rho$  is a reaction constant such that  $-\rho\sigma'$  gives the effect of the substituent on the enthalpy of activation. Substituting the rate constant expressions in the definition of  $\sigma$ , and assuming the transmission coefficients to be unity,<sup>22</sup> or at least to cancel

$$\sigma = \frac{\Delta S_i - \Delta S_i^0}{2.3R} + \frac{2\rho\sigma'}{2.3RT} \quad (4)$$

where  $\Delta S_i$  and  $\Delta S_i^0$  are entropies of ionization, i.e.,  $\Delta S_i^\ddagger - \Delta S_r^\ddagger$ . By defining  $\rho = 1$  for the substituted benzoic acid ionization reaction, and making the usual assumption that entropies of ionization are the same for substituted acids as for the unsubstituted,  $\sigma = 2\sigma'/2.3RT$ . Analogous equations are obtained if  $\sigma$  is determined from the influence of the substituent on the rate of a reaction, the entropy term in eq. 4 then becoming  $\Delta S_i^\ddagger - \Delta S_u^\ddagger$  the difference in the entropies of activation

(22) Another terminology can be based on the relation between partial ionic character of a bond and the electronegativity difference of the bonded atoms.  $\delta$ -Values and thereby  $\sigma$ -values can be interpreted as expressing the influence of substituents on the partial ionic character of the corresponding bonds in the molecule.

(23) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

of substituted and unsubstituted reactants; also, the last term in eq. 4 becomes  $\rho\sigma'/2.3RT$  since the rate constant in only one direction enters the derivation.

It was suggested earlier<sup>24</sup> that the differences between  $\sigma$  and  $\delta$  might be caused by the effects of substituents on the entropies of activation. In eq. 4,  $\delta$  should be related directly only to  $\sigma'$ . Any entropy differences would combine with the  $\sigma'$  term to give the observed  $\sigma$ , but would not contribute to  $\delta$ . However, the relatively few reported experimental entropy differences<sup>24</sup> are generally too small and not systematic enough to explain the recent observations. Still, some of the deviations may be attributed in part to entropy effects.

Another way in which the normal molecule differs from the transition state is the polarization of the molecule by the attacking group. Transmission of polarizability effects to the meta position is by the relatively poor inductive mechanism, while the much stronger resonance, or electromeric, mechanism operates at the ortho and para positions. At first glance, this might appear to account for the different meta and para curves. Unfortunately for the present purpose, the polarizability and static electromeric effects are in the same direction.<sup>10b</sup> So the  $\sigma_p/\delta_p$  ratio should be larger than the  $\sigma_m/\delta_m$  ratio, since  $\sigma_p$  incorporates both effects while  $\sigma_m$  and both  $\delta$ -values depend primarily on the static effect. Actually, the reverse is true.

Thus, it does not appear that the main  $\sigma,\delta$  differences can be ascribed to transition *versus* normal state differences; so normal state effects would appear responsible. A great deal of indirect evidence<sup>10</sup> indicates that substituents influence the meta position chiefly by the inductive mechanism, the para by the electromeric, and the ortho by a combination of inductive, electromeric and steric mechanisms. There is no basis in Ramsey's theory of nuclear magnetic shielding,<sup>8</sup> or otherwise, for supposing that the fundamentally different inductive and electromeric effects would produce changes in  $\delta$  in a ratio identical to the changes in  $\sigma$ . In fact, it may be concluded that the separate meta and para curves are a direct demonstration of the different character of the main electronic effects at the meta and the para positions. The smaller slope of the para curve then means that the electromeric effects change  $\delta$  relatively more than  $\sigma$ , as compared to the inductive effects. Fortunately, this is consistent with the para intercept. All substituents other than hydrogen have  $\pi$  or unshared  $p$ -electrons and therefore produce electromeric effects at the ortho and para positions. The  $\sigma_p$  zero value corresponds to a balance of opposing inductive (+I) and electromeric (-E) effects.<sup>25</sup> However, for  $\delta_p$  the electromeric effect is larger than the inductive, with a resultant negative  $\delta_p$ , as observed. The inductive effect must be positive for  $\sigma_p = 0$  because the substituents for which  $\sigma_p$  is about zero have positive  $\sigma_m$  values.

(24) See reference 10c, pages 84 and 121 for typical values.

(25) Following Dewar, reference 10b, the signs of the  $E$  and  $I$  effects are defined to correspond to the charges produced on the benzene ring by the substituent. These agree also with the signs of  $\sigma$  and  $\delta$ . The usage of "electromeric" to include static as well as dynamic effects is also that of Dewar.

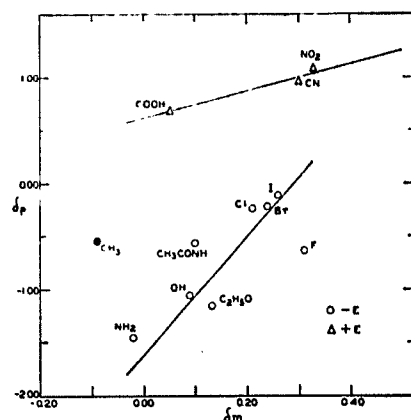


Fig. 4.—A plot of  $\delta_p$ -versus  $\delta_m$ -values for substituted benzenes.

**Interdependence of the  $\delta$ -Values.**—In Fig. 4, the  $\delta_p$ -values are plotted against the  $\delta_m$ -values for the same substituent. It is seen that the data fall into two distinct classes, in each of which  $\delta_p$  is roughly proportional to  $\delta_m$ . The  $\text{CH}_3$  group stands somewhat alone. In Fig. 5 the  $\delta_p$ -values are plotted against the  $\delta_o$ . The same substituents are demonstrated clearly to be divided into the same two classes. Also, it is evident that the  $\text{CH}_3$  group falls in the class with the halogens and other substituents without multiple bonds. The six  $\delta_p$ -values in Table I for which the corresponding  $\delta_m$ -values have not been observed follow the same rules as those in Fig. 4, insofar as the  $\delta_m$ -values can be estimated from the observed  $\sigma_m$ .

Several conclusions can be drawn from the results graphically presented in the two figures. The electromeric effects are generally proportional to the inductive. This follows from the approximate linearity of both  $\delta_p$ - $\delta_m$  curves and their positive slopes, in conjunction with the previous conclusion that  $\delta_p$ -values are determined mainly by electromeric effects and  $\delta_m$ , by inductive. The separate curves prove the existence of two different types of electromeric interaction. The class with negative  $\delta_p$ -values includes only substituents with unshared  $p$ -electrons; these substituents have been considered generally<sup>10b</sup> to be  $-E$  electromeric in nature. The class with positive  $\delta_p$ -values includes all substituents with  $\pi$ -electrons,  $\text{NO}_2$ ,  $\text{CN}$  and  $\text{COOH}$ , the  $+E$  substituents.

The  $\delta_p$ - $\delta_o$  curve in Fig. 5 for  $-E$  substituents supports the view that both the  $E$  and the  $I$  interactions are more important at the ortho than each is, respectively, at the para and meta positions. For example,  $\text{NH}_2$  has the weakest  $I$  effect, with a  $\delta_m$  of  $-0.02$ , so the  $\delta_o$ -value of  $-2.31$  is mainly the  $-E$  effect. This is to be compared with the  $\delta_p$ -value for  $\text{NH}_2$  of  $-1.46$ . As the  $+I$  character of the  $-E$  substituents increases, the  $\delta_o$ -values become proportionately more positive compared to the  $\delta_p$ . The methyl group is anomalous again; it is  $-I$ , yet the  $\delta_o$ -value is even more positive than many of the substituents which are  $+I$ . The fluorine substituent with its relatively large  $+I$  effect presents another anomaly in its large negative  $\delta_o$ -value compared to its value for  $\delta_p$ .

The  $\delta_p$ - $\delta_o$  curve in Fig. 5 for  $+E$  substituents is

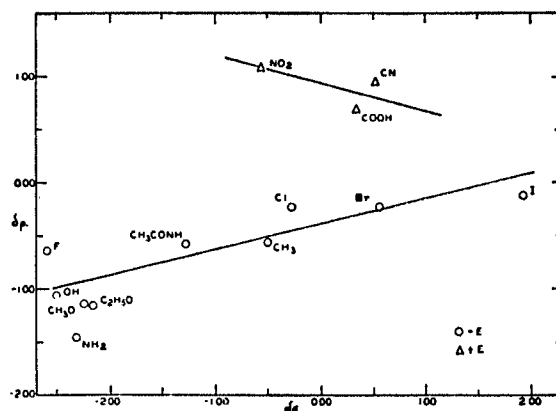


Fig. 5.—A plot of  $\delta_p$ -versus  $\delta_o$ -values for substituted benzenes.

also exceptional. The  $+E$  substituents exhibit  $+I$  interactions, as is seen from the positive  $\delta_m$ -values in Fig. 4. However,  $\delta_o$ - $\text{NO}_2$  is *negative* and the  $\delta_o$ -values for  $\text{COOH}$  and  $\text{CN}$  are *less than* the  $\delta_p$ -values. The implication is that these substituents have some variety of negative effect on  $\delta$  which falls off much more rapidly than do the  $+I$  and  $+E$  upon going from the ortho to the meta and para positions. The methyl group is a  $-I$ ,  $-E$  substituent and exhibits a similar but positive effect at the ortho position. This question will be discussed in more detail in the section on the halogen derivatives.

The interdependence of the  $\delta$ -values is related also to the differences in the behavior of the  $\sigma$ - and  $\delta$ -values discussed above. If one plots  $\sigma_p$  versus  $\sigma_m$ , a fairly good single line is obtained. The contrasting fact that  $+E$  substituents have a separate  $\delta_p$ - $\delta_m$  curve, with larger, positive, values than the  $-E$ , supports the conclusion of the previous section that  $E$  interactions change  $\delta$  proportionately more than do  $I$  interactions. The scatter of points from the  $\delta_p$ - $\delta_m$  curves indicates varying proportions of  $I$  and  $E$  interactions, which in turn show up in deviations from the  $\sigma$ - $\delta$  curves.

**$\delta$ -Values for the Halogens.**—The  $\delta$ -values of the halogens suggest differences from the other  $-E$  substituents. In Fig. 6, there is shown the dependence of the  $\delta$ -values on the electronegativity of the halogen; the  $\sigma_m$  and  $\sigma_p$  data are included for comparison. The main point of interest is the  $\delta_o$  curve, in which  $\delta_o$  becomes more positive in the sequence  $\text{F}$ ,  $\text{Cl}$ ,  $\text{Br}$  and  $\text{I}$  with  $\delta_o$ -values of  $-2.59$  and  $+1.93$  for fluorine and iodine, respectively. The  $+I$  effects depend on the electron affinity of the halogen and decrease in the order  $\text{F} > \text{Cl} > \text{Br} > \text{I}$ . The  $-E$  effects depend ordinarily on the ionization energy and on this basis would decrease in magnitude in the order  $\text{I} > \text{Br} > \text{Cl} > \text{F}$ .

According to this argument, iodine has the weakest  $+I$  and the strongest  $-E$  effects, and therefore the strongest net negative substituent effect of the halogens. Actually the  $\delta$ -values, as well as the  $\sigma$ , show that the  $-E$  effects are reversed for the halogens,<sup>28</sup> decreasing in the same order as

(28) See, e.g., A. E. Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, and articles cited therein.

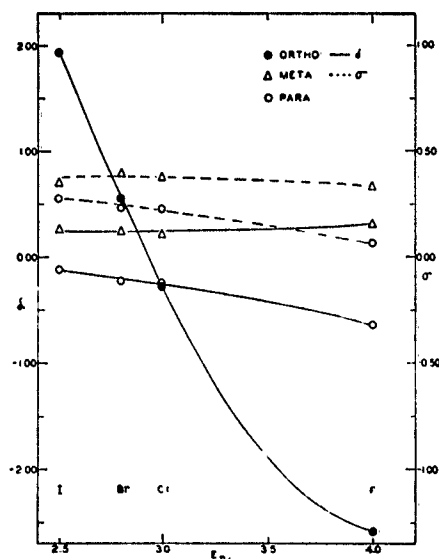


Fig. 6.— $\delta_o$ - and  $\sigma$ -values compared with the electronegativity of the halogens.

the  $+I$  effects,  $F > Cl > Br > I$ . With the two effects in opposing directions but in the same order, then by varying their relative magnitudes, almost any desired sequence of resultant effect can be obtained.<sup>27</sup> The justification given for reversing the order of the  $-E$  effects is that the larger atoms, particularly those past the first row, do not readily increase their covalencies,<sup>28</sup> as required for the  $-E$  effect.

The  $\delta_m$ - and  $\delta_p$ -values are in partial accord with this argument. It has been remarked in the discussion of the  $\delta_p$  versus  $\delta_m$  plot in Fig. 4 that fluorine appeared somewhat anomalous, being separated from the other halogens. It has the largest  $\delta_m$ -value ( $+I$ ) and yet the largest negative  $\delta_p$ -value ( $-E$ ), as predicted. However, the positive  $\delta_m$ -values for the other halogens are  $I > Br > Cl$ , the reverse of the predicted  $+I$  order. And then, there is the previously noted exceptionally large  $\delta_o$ -value for iodine. These observations are incompatible with the small range, from  $-0.24$  to  $-0.12$  in  $\delta_p$  on going from chlorine to iodine. The indicated small corresponding range in  $-E$  effects cannot account for the change in  $\delta_o$  from  $-0.27$  to  $+1.93$ ; and the predicted direction of the  $+I$  sequence,  $Cl > Br > I$ , is the reverse of that required to explain the trend in  $\delta_o$ .

Thus, there seems to be an additional positive  $\delta_o$ -interaction for the halogens in order  $I > Br > Cl > F$ , similar perhaps to that noted above for the  $+E$  substituents and for  $CH_3$ . This  $\delta_o$ -interaction may be electromeric in nature since, when present, its sign is opposite to that of the usual electromeric effect, while there is no such correlation with the inductive effect. There are several mechanisms possible, but there is not sufficient evidence for a critical choice. However, at least in the case of the halogens, the usual sorts of interaction would

(27) J. F. J. Dippy and R. H. Lewis, *J. Chem. Soc.*, 644 (1936).

(28) Recently, K. S. Pitzer, *THIS JOURNAL*, **70**, 2140 (1948), has given an interesting discussion of this effect in terms of inner electron shell repulsions.

appear to give a negative rather than a positive effect, or else be in the wrong sequence. One way in which the halogens might withdraw electrons selectively from the ortho position is by a small overlap of the vacant low-lying  $d$ -orbitals of the halogen with the  $\pi$ -orbitals in benzene. This would give the sequence  $I > Br > Cl$  since the  $d$ -orbitals are lowest lying for iodine, and absent of course in the valence shell of fluorine.

**$\delta_o$ -Values and Entropy Effects.**—The hope was voiced earlier<sup>29</sup> that  $\delta_o$ -values in combination with rate or equilibrium constants would permit evaluation of the entropy terms. Thus, if  $\delta_o$  could be related directly to  $\sigma'$  in eq. 4, and the reaction constant  $\rho$  applied to ortho as well as meta and para substituents, then experimental rate or equilibrium constants could be used to compute entropies of activation or of ionization. It is now clear, however, that the varying influence on  $\delta$  of the several electronic interactions severely limits such an approach. Nonetheless, it may be of some interest to give a comparison of  $\delta_o$  with several " $\sigma_o$ "-values, where the " $\sigma_o$ "-values are obtained in the same way as  $\sigma_m$  and  $\sigma_p$ , from the influence of an ortho substituent on a rate or equilibrium constant.

Values of " $\sigma_o$ " were obtained from the equation " $\sigma_o$ " =  $(1/\rho) \log (K/K_u)$  using Dippy's tabulation<sup>13</sup> of dissociation constants, which includes a limited number of ortho-substituted benzoic and phenylacetic acids and the  $o$ -halophenols. Reaction constant  $\rho$ 's of  $+1.00$ ,  $+0.47$  and  $+2.01$ , respectively,<sup>10c</sup> were used for the three series of compounds. The resulting values of " $\sigma_o$ " are plotted in Fig. 7 against the  $\delta_o$ -values. It is seen that the data for the halogens fall upon separate smooth curves for the three series of compounds. The parallelism and large separation of the curves suggests an interaction between the ortho substituents and the reacting group,<sup>10a</sup> the interaction being characteristic of the reacting group and relatively insensitive to the particular halogen.

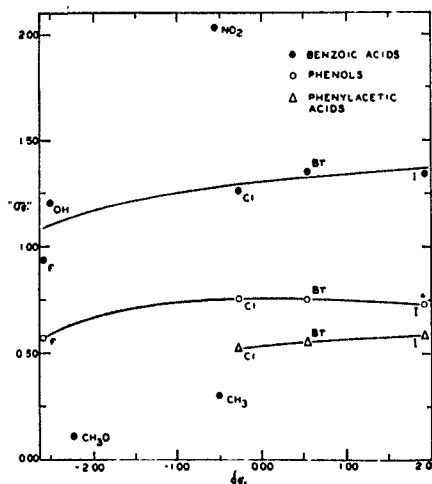


Fig. 7.—A comparison of  $\delta_o$ -values with " $\sigma_o$ "-values calculated from the effect of ortho substituents on dissociation constants.

Data for other substituents are limited mainly to the benzoic acids. The point for OH in Fig. 7



lies fairly well on the same curve as the halogens, probably accidentally; however, the  $\text{CH}_3\text{O}$ ,  $\text{CH}_3$  and  $\text{NO}_2$  points are scattered widely. The relative magnitudes of entropy and electronic effects in these deviations from a smooth " $\sigma_o$ "- $\delta_o$  curve are not separable at present, but it does seem reasonable that if two substituents are very similar in their electronic effects, then any deviations in their " $\sigma_o$ "-values arise mainly from entropy effects. For instance, the  $\delta$ -values for OH,  $\text{CH}_3\text{O}$  and  $\text{C}_2\text{H}_5\text{O}$  are nearly identical for each of the three positions, yet " $\sigma_o$ " for OH is +1.20 and for  $\text{CH}_3\text{O}$ , +0.30. Ascribing the " $\sigma_o$ " difference to the entropy term in eq. 4,  $\Delta S_i$  for the *o*-hydroxybenzoic acid is about 4 e.u. larger than for the *o*-methoxybenzoic acid. This is in the wrong direction to be a steric effect of the larger  $\text{CH}_3\text{O}$  group and, instead, chelation of the OH group with the  $\text{CO}_2^-$  anion is indicated, as proposed by Branch<sup>10a</sup> and reviewed by Dippy.<sup>13</sup> A detailed general analysis of the  $\delta_o$ -values requires more experimental dissociation or rate constants and entropies than are presently available.

**Other Substituent Parameters Compared to  $\delta$ .**—Most of the other numerical substituent parameters are correlated to some degree with the  $\sigma$ -values and therefore with the  $\delta$ -values. Price<sup>29</sup> has used  $\Delta\sigma = \sigma_p - \sigma_m$  as a measure of electromeric effects, the negative  $\sigma_m$  term correcting for the small amount of inductive effect at the para position. A plot of  $\Delta\sigma$  versus  $\Delta\delta$  shows separate lines for the +*E* and -*E* substituents, related to those in Fig. 4.  $\Delta\delta$  is defined as  $\delta_p - \delta_m$ , by analogy to  $\Delta\sigma$ ; however, since  $\delta_p$  is primarily electromeric, it alone gives nearly as good correlations as  $\Delta\delta$ . Very similar results are obtained upon comparing  $\delta_p$  or  $\Delta\delta$  with the  $\Delta\lambda_{\text{calcd.}}$  of Doub and Vandenberg.<sup>30</sup> In Fig. 8, the substituent spectroscopic moments of Platt<sup>14</sup> are plotted against  $\Delta\delta$ . In this case, the data for +*E* as well as -*E* substituents appear to be along a single straight line.

Another parameter of considerable potential interest is the influence of a substituent on the chlorine quadrupole coupling constants in substituted chlorobenzenes. Preliminary results of this sort at Harvard,<sup>31</sup> and similar work started independently here at a later time, suggest a single linear relation between the coupling constants and the meta and para  $\sigma$ 's.

### Polysubstituted Benzene Derivatives

Polysubstituted fluorobenzenes were investigated primarily to determine the extent to which the substituent effects are additive. No previous attempt seems to have resulted in a systematic quantitative analysis of the problem.<sup>32</sup> Remick<sup>28</sup> reviews the question in some detail and cites results suggesting in several cases that interactions between substituents alter their relative directive powers.

The  $\delta$ -values observed in a number of polysubstituted fluorobenzenes are listed in the first numerical column of Table II. The next column

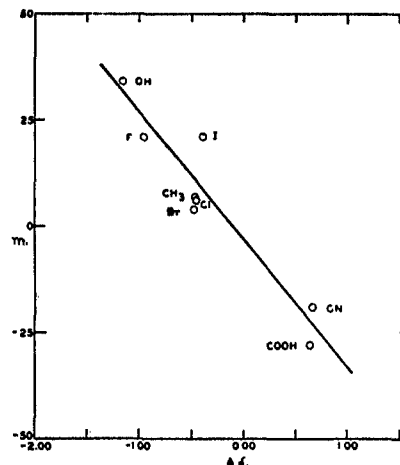


Fig. 8.—A comparison of  $\Delta\delta = \delta_p - \delta_m$  with the substituent spectroscopic moment of Platt.

lists predicted  $\delta$ 's, the sums of the  $\delta$ -values from Table I for the individual substituents. The thirty-eight complete entries in Table II represent twenty-four polysubstituted fluorobenzenes; the designations of substituents follows the convention that the observed fluorine is at the 1-position. Entries for different fluorines in the same compound are enclosed by brackets. It was possible to assign the observed  $\delta$ -values to the different fluorines by comparison with the predicted values. The last column in Table II is  $(\delta_{\text{obsd}} - \delta_{\text{pred}})$ , a quantitative measure of non-additivity of the substituent effects.

It is seen that deviations from additivity do occur frequently but that they are generally fairly small. The sum of the absolute values of the deviation is 5.06, and of  $\delta_{\text{pred}}$ , 42.27. The probable errors of each experimental  $\delta$  is conservatively  $\pm 0.03$ . Applying the theory of error propagation, the average fractional deviation from additivity, exclusive of experimental error, is somewhere between 6 to 12%. The 5.06 deviation sum represents ninety individual  $\delta$ -values so the average non-additivity per substituent is only from 0.03 to 0.06  $\delta$ -unit. The root mean square deviation per compound, including experimental error, is  $\pm 0.17$ .

The arithmetic sum of the deviations is +3.56 or an average value per compound of +0.10, demonstrating that the observed  $\delta$  is generally larger than that predicted. Only seven of the deviations are negative. The sum of the  $\delta_{\text{pred}}$  is -27.55, with only eleven of the values positive, suggesting a general correlation between the net negative direction of the substituent effects and the positive deviations from additivity. The several large deviations demonstrate significant interactions among the substituents, but a systematic analysis of more compounds appears necessary to disclose the conditions required for interaction. It should be pointed out that the existence of substituent interactions may have some bearing on the  $\sigma$ - $\delta$  relations discussed above.  $\delta$  is evaluated by comparing fluorobenzene with a substituted fluorobenzene, and any interaction between the substituent and the fluorine would not need to be the same as that between fluorine and the hydrogen in the unsubstituted fluorobenzene.

(29) C. C. Price, *Chem. Revs.*, **30**, 37 (1941).

(30) L. Doub and J. M. Vandenberg, *This Journal*, **69**, 2714 (1947); *ibid.*, **71**, 2414 (1949).

(31) Private communication, E. B. Wilson, Jr.

(32) See, for example, reference 10b, p. 165, and papers cited therein.

TABLE II  
 $\delta$ -VALUES FOR POLYSUBSTITUTED BENZENE DERIVATIVES

Substituents <sup>a</sup>	$\delta$ observed	$\delta$ predicted	Deviation ( $\delta_{\text{obsd}} - \delta_{\text{pred}}$ )
3-NO <sub>2</sub> ,4-NH <sub>2</sub> <sup>b</sup>	-1.43	-1.13	-0.30
2-NO <sub>2</sub> ,4-NH <sub>2</sub> <sup>b</sup>	-2.16	-2.02	-.14
3,5-DiF	+0.55	+0.62	-.07
3-F,5-I	+ .45	+ .57	-.12
2,4-DiNO <sub>2</sub>	+ .54	+ .52	+.02
2-NH <sub>2</sub> ,4-F	-2.87	-2.95	+.08
3-NH <sub>2</sub> ,4-F	-0.58	-0.66	+.08
2-NH <sub>2</sub> ,5-F	-1.83	-2.00	+.17
3-F,4-NH <sub>2</sub>	-1.15	-1.15	.00
2-NO <sub>2</sub> ,4-F	-1.03	-1.20	+.17
3-NO <sub>2</sub> ,4-F	-0.20	-0.31	+.11
2-NO <sub>2</sub> ,5-F	+ .11	-0.25	+.36
3-F,4-NO <sub>2</sub>	+1.49	+1.39	+.10
2,4-DiF	-3.04	-3.23	+.19
3,4-DiF	-0.24	-0.33	+.09
2,5-DiF	-2.09	-2.28	+.19
2-Cl,4-F	-0.86	-0.91	+.05
3-Cl,4-F	-.39	-.43	+.04
2-Cl,5-F	+ .20	+ .04	+.16
3-F,4-Cl	+ .20	+ .07	+.13
2-Br,4-F	-.08	-.09	+.01
3-Br,4-F	-.40	-.40	.00
2-I,4-F	+1.23	+1.29	-.06
3-I,4-F	-0.45	-0.38	-.07
2-I,5-F	+2.36	+2.24	+.12
3-F,4-I	+0.30	+0.19	+.11
2-CF <sub>3</sub> ,4-F	-.74	....	....
3-CF <sub>3</sub> ,4-F	-.40	-0.36	-.04
2,4,6-TriCH <sub>3</sub>	-1.50	-1.55	+.05
2,5-DiCl,4-F	-0.55	-0.70	+.15
2,5-DiBr,4-F	+ .22	+ .15	+.07
2,4,5-TriF	-2.67	-2.92	+.25
2-Br,4,5-DiF	+0.43	+0.22	+.21
2,4-DiF,5-Br	-2.75	-2.99	+.24
2,5-DiF,4-Br	-2.06	-2.51	+.45
2,5-DiF,3-CF <sub>3</sub>	-1.77	-2.00	+.23
2,4-DiF,6-CF <sub>3</sub>	-3.20	....	....
3,4-DiF,5-CF <sub>3</sub>	+0.07	-0.05	+.12
2,4,6-TriCH <sub>3</sub> ,3-F	-.96	-1.24	+.28
2,4,6-TriCH <sub>3</sub> ,3,5-DiF	-.90	-0.93	+.03

<sup>a</sup> The designation of substituents follows the convention that the observed fluorine is at the 1-position. <sup>b</sup> In nitrobenzene solution.

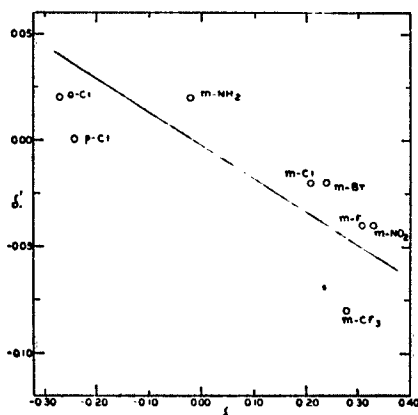


Fig. 9.—A comparison of substituent effects in substituted benzotrifluorides,  $\delta'$ , with those in fluorobenzene,  $\delta$ .

The  $\delta$ -values for the polysubstituted benzenes might be used to investigate the transmission mechanism of the substituent effects. The inductive effect, particularly, could operate directly through space as well as *via* the benzene nucleus. If this be so, an ortho substituent could block at least partially the direct inductive effect of an adjacent meta substituent. However, as yet not enough compounds of this type have been measured for any conclusions to be drawn.

#### Monosubstituted Benzotrifluorides

Several  $\delta'$ -values, for monosubstituted benzotrifluorides, are listed in Table III. These give the influence on the fluorines in the CF<sub>3</sub> group of substituents in the benzene ring. A comparison of the  $\delta'$ - with the  $\delta$ -values for the same substituents reveals two interesting results. The  $\delta'$ -values are only about a tenth of the  $\delta$ ; moreover, the sign of  $\delta'$  is the reverse of  $\delta$ . This may be seen by the negative slope in Fig. 9, in which the data are plotted.

TABLE III

$\delta'$ -VALUES FOR MONOSUBSTITUTED BENZOTRIFLUORIDES

Substituent	$\delta'$	$\delta$	Substituent	$\delta'$	$\delta$
<i>o</i> -Cl	+0.02	-0.27	<i>p</i> -CF <sub>3</sub>	-0.08	....
<i>m</i> -Cl	-.02	+.21	<i>o</i> -NH <sub>2</sub>	+.02	-2.31
<i>p</i> -Cl	.00	-.24	<i>m</i> -NH <sub>2</sub>	+.02	-0.02
<i>o</i> -CF <sub>3</sub>	+.33	....	<i>m</i> -F	-.04	+.31
<i>m</i> -CF <sub>3</sub>	-.08	+.28	<i>m</i> -Br	-.02	+.24
			<i>m</i> -NO <sub>2</sub>	-.04	+.33

Most of the tabulated  $\delta'$ -values are not much larger than experimental error. However, the fact that *all* of the  $\delta'$ -values are of sign opposite to the corresponding  $\delta$  is strong evidence that the sign reversal is real. The tenfold attenuation and the sign reversal may depend to some extent on differing behavior of  $\delta'$  and  $\delta$  to electron distribution in the two types of compounds. Still, the indicated extension of the  $\delta$ -parameter to classes of compounds other than substituted fluorobenzenes has widespread potentialities.

One  $\delta'$ -value of particular immediate interest is that for *o*-CF<sub>3</sub>-benzotrifluoride. It is +0.33 compared to -0.08 for the *m*- and *p*-isomers and from -0.04 to +0.02 for the other eight compounds in Table III. The CF<sub>3</sub> groups ortho to each other are close enough to cause direct interaction between the fluorines. The closest distance of approach of the fluorines in the adjacent groups is about 1.50 Å., and the greatest separation, 1.65 Å., which are to be compared with the accepted fluorine van der Waals radius of 1.35 Å. The high  $\delta'$ -value appears to be further evidence of the large fluorine-fluorine repulsions postulated to account for molecular distortion in various cyclofluorocarbons.<sup>22</sup>

#### General Comments

The utility of nuclear magnetic shielding data is discussed above. In addition, it should be pointed out that relatively few nuclei are well suited for this type of experiment. The requirements are: a nuclear spin of 1/2 to avoid quadru-

(33) See W. L. Roth in "Annual Review of Physical Chemistry" Annual Reviews, Inc., Stanford, California, 1951, p. 222.

polar broadening; a large enough magnetic moment and isotopic abundance to give observable absorption; at least a moderate atomic number so there are measurable changes in magnetic shielding with compound; and, finally, chemical properties such that enough compounds are available for a more or less empirical analysis. Nuclei meeting these requirements are  $F^{19}$ ,  $P^{31}$  and  $H^1$ , in decreasing order on a rough, over-all basis. On the other hand, of the nuclei unsuitable for magnetic shielding measurements because they have spins greater than  $1/2$ , several have electric quadrupole moments of a convenient size for determining quadrupole coupling constants.<sup>2</sup> These include the other halogens and nitrogen, with the latter of particular interest in connection with electron distribution in double

bonds. So either the nuclear magnetic or quadrupole radiofrequency spectrum can be observed for a considerable number of nuclei, and thereby a wide variety of problems in molecular electronic distribution can be investigated.

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## Nuclear Magnetic Resonance in Metals. I. Broadening of Absorption Lines by Spin-Lattice Interactions\*†

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Magnetic resonance line shapes and widths, their temperature dependence, and the conduction electron shifts in resonance frequency are reported for the metals Li<sup>7</sup>, Na<sup>23</sup>, Al<sup>27</sup>, Cu<sup>63</sup>, Cu<sup>65</sup>, Ga<sup>69</sup>, Ga<sup>71</sup>, Rb<sup>85</sup>, Rb<sup>87</sup>, and Cs<sup>133</sup>. The absorption lines in most of these metals are broader than predicted for nuclear magnetic dipolar broadening alone. We propose that the mechanism responsible for most, if not all, of this additional broadening is the interaction between the nuclear spins and the conduction electrons, which also determines the spin-lattice relaxation time. Spin-lattice relaxation times  $T_1$  are estimated from the nondipolar broadening of the experimental absorption lines. These  $T_1$  values compare favorably with available directly measured values and with approximate  $T_1$  values obtained by Korringa's theory from the measured resonance shifts. In the case of lithium, a dipolar line-width transition was observed at 255°K; this transition results from self-diffusion, for which we determine an activation energy of  $9.8 \pm 1$  kcal/mole.

### INTRODUCTION

IT was noted in a preliminary letter<sup>1</sup> that nuclear magnetic resonance absorption lines in metals were broader than could be explained by Van Vleck's<sup>2</sup> theory of dipolar broadening. The experimental second moments for the absorption lines of Na<sup>23</sup>, Al<sup>27</sup>, Cu<sup>63</sup>, and Cu<sup>65</sup> were greater than predicted. Bloembergen<sup>3</sup> observed earlier that the line widths for Cu<sup>63</sup> and Cu<sup>65</sup> were rather large in the metals but made no detailed analysis and concluded the results were within experimental error of expectation. More recently, Knight<sup>4</sup> has reported that the line widths of V<sup>51</sup> and Cr<sup>53</sup> exceed the values estimated from the nuclear magnetic dipolar broadening alone. The resonance frequencies are known<sup>5</sup> to be higher in metals than in their compounds by up to several tenths of a percent, owing to<sup>6</sup> the contribution of the conduction electrons to the magnetic field at the nuclei in the metal. Anisotropy in these conduction electron shifts might lead to line broadening<sup>1</sup> in the metals; so could quadrupolar coupling in case the cubic symmetry of the electric field in the crystal lattice was disturbed in some manner.<sup>1,4</sup> The research described herein characterizes the major aspects of the line broadening effect and provides convincing evidence that it is a consequence of the strong interactions of the nuclear spins with the conduction electrons, which are responsible also for the very short spin-lattice relaxation time.

Heitler and Teller<sup>7</sup> first pointed out the importance of the conduction electrons in metals in determining

the relaxation time for the transfer of energy between a nucleus and its surroundings. Korringa<sup>8</sup> has related the spin-lattice relaxation time  $T_1$  to the conduction electron shift in resonance frequency,  $\Delta H/H$ . Korringa's final result<sup>9</sup> is

$$T_1(\Delta H/H)^2 = \hbar / \pi k T g^2. \quad (1)$$

$g$  is here the nuclear gyromagnetic ratio in Bohr magnetons. Typical values for  $T_1$  in metals are the order of  $10^{-4}$  sec compared to values of  $10^{-2}$  to  $10^4$  sec for chemical compounds. The significance of this may be seen from the approximate equation<sup>10</sup> relating the inverse line-width parameter  $T_2$  to the spin-spin interaction parameter  $T_2'$ , and the spin-lattice relaxation time  $T_1$ ,

$$(1/T_2) \cong (1/T_2') + (1/2T_1). \quad (2)$$

In most solids,  $T_1$  is of such magnitude that the associated effect upon the shape and width of the resonance line is negligible, but in systems where the spin-lattice relaxation time is exceptionally short, the relaxation interaction can broaden the absorption line appreciably. This has been verified experimentally in solutions of paramagnetic salts.<sup>10</sup> The line broadening in the metals is interpreted in a similar fashion.

### EXPERIMENTAL PROCEDURE

The particular apparatus and some of the methods have been described previously.<sup>11,12</sup> All experiments were at an applied magnetic field of  $6365 \pm 2$  gauss. Measurements included line shapes and widths, their temperature dependence, and the conduction electron shifts in resonance frequency.

A radiofrequency bridge system<sup>10</sup> was used with a signal generator, preamplifier, and receiver tuned at

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† A report of this work was given at the Washington meeting of the American Physical Society, May, 1952; Phys. Rev. 87, 226(A) (1952).

‡ AEC Predoctoral Fellow.

<sup>1</sup> H. S. Gutowsky, Phys. Rev. 83, 1073 (1951).

<sup>2</sup> J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).

<sup>3</sup> N. Bloembergen, Physica 15, 588 (1949).

<sup>4</sup> W. D. Knight, Phys. Rev. 85, 762(A) (1952).

<sup>5</sup> W. D. Knight, Phys. Rev. 76, 1259 (1949).

<sup>6</sup> Townes, Herring, and Knight, Phys. Rev. 77, 852 (1950).

<sup>7</sup> W. Heitler and E. Teller, Proc. Roy. Soc. (London) A155, 637 (1936).

<sup>8</sup> J. Korringa, Physica 16, 601 (1950).

<sup>9</sup> C. P. Slichter independently obtained the same equation by an approximate method in some unpublished research.

<sup>10</sup> Bloembergen, Purcell, and Pound, Phys. Rev. 73, 679 (1948).

<sup>11</sup> H. S. Gutowsky and C. J. Hoffman, J. Chem. Phys. 19, 1259 (1951).

<sup>12</sup> Gutowsky, McClure, and Hoffman, Phys. Rev. 81, 635 (1951).

the resonance frequency. Null-T bridges<sup>13</sup> were found more convenient than the Purcell type<sup>10</sup> at lower frequencies. Line shapes were obtained by modulating the magnetic field at 30 cycles with an amplitude a small fraction of the line width. A plot of the output with a narrow band amplifier gave the derivative of the absorption line as the magnetic field applied to the sample was varied over the necessary range. Line widths  $\delta H$  are taken to be the separation of the two peaks on the derivative curves. A typical plot of the derivative curve for the  $\text{Cu}^{63}$  resonance is given in Fig. 1. Experimental second moments were obtained by integrating<sup>14</sup> the curves. The reported values are the averages of from five to nine separate plots. The maximum error in the second moments is approximately 6 to 8 percent. The estimated error in the line widths is about 3 percent for the broad lines and 6 percent for the much narrower lines of rubidium, cesium, and gallium. An additional error is present in the measurement of the narrow lines due to broadening by field inhomogeneities and modulation effects, which contribute between 0.05 and 0.10 gauss to the apparent line widths.

Metals investigated included lithium, sodium, aluminum, copper, gallium, rubidium, and cesium. The samples were obtained commercially and used without further purification. The resonance absorption occurs in the surface of the metal to the skin depth, so it is necessary to have very small particles to obtain maximum intensities. In the case of the alkali metals, the samples were dispersions of the metal in white mineral oil. The sodium dispersion is available commercially and has been described.<sup>1</sup> The others were made by heating a mixture of the metal and mineral oil above the melting point of the metal and agitating the mixture with a high speed stirrer. A dry nitrogen atmosphere was used to prevent oxidation. The stirring was continued as the dispersion was cooled until the metal particles solidified. This method gave a satisfactory particle size, and the dispersions showed no tendency to coagulate even when they were heated above the melt-

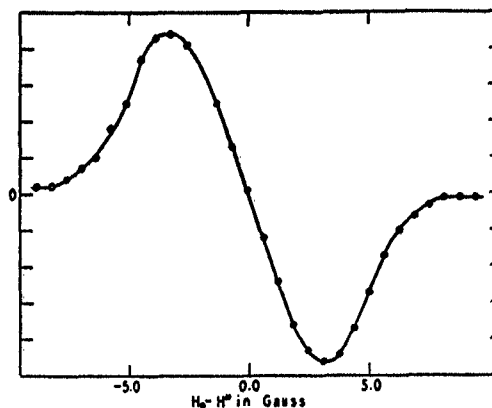


FIG. 1. The derivative of the  $\text{Cu}^{63}$  magnetic resonance absorption line at 298°K. The line width  $\delta H$  is 6.4 gauss, and the second moment  $\Delta H^2$  is 6.3 gauss<sup>2</sup>.

ing point of the metal. Aluminum and copper were fine powders; the oxide coating of the particles was sufficient insulation to permit their use without further treatment. The gallium was dispersed in mineral oil by shaking it by hand in a test tube; oleic acid was added as an anticoagulant.

An all-metal cryostat operating on the principle of a variable heat leak<sup>11</sup> was used for the experiments on the temperature dependence of line widths and second moments. The temperatures were measured with a copper-constantan thermocouple immersed directly in the sample. The resonance line shifts between the metals and their compounds were measured by two methods, depending on the magnitude of the shift. For aluminum, copper, lithium, and sodium, whose shifts are small, the shift was found by measuring the difference in applied magnetic field needed to center the resonance line of the metal and of the salt, alternately, when either was placed in the same coil, the frequency being kept constant.<sup>11</sup> For rubidium, cesium, and gallium, whose shifts are much larger, the applied field was kept constant and the frequency of the signal generator varied to center the resonance line for a given sample. The frequency of the signal generator was then measured by zero beating its signal with that of a BC-221 Signal Corps frequency meter set by reference to WWV. The errors in the observed resonance shifts are about  $\pm 1$  percent of the measured values.

## RESULTS AND DISCUSSION

### Resonance Shift in the Metals

The resonance shifts observed for the metals at room temperature (298°K) are given in Table I along with the values reported by Knight.<sup>5,6,15</sup> The agreement between the two sets of data is quite good. The entries preceded by the sign  $\sim$  are preliminary, approximate values.<sup>15</sup> All of the shifts measured by us were with respect to aqueous solutions of the salts except for

TABLE I. Shifts in the nuclear magnetic resonance frequencies of metals compared to their compounds, at room temperature.

Nucleus	Compound <sup>a</sup>	$\Delta H/H$ This research	$\Delta H/H$ Knight
$\text{Li}^7$	$\text{LiNO}_3^b$	$0.0261 \pm 0.0002 \times 10^{-2}$	$\sim 0.02^b \times 10^{-2}$
$\text{Na}^{23}$	$\text{NaOH}$	$0.112 \pm 0.001$	$0.10^c$
$\text{Al}^{27}$	$\text{AlCl}_3$	$0.161 \pm 0.001$	$0.16^c$
$\text{Cu}^{63}$	$\text{CuBr}^c$	$0.237 \pm 0.001$	$0.23^c$
$\text{Cu}^{65}$	$\text{CuBr}^c$	$0.235 \pm 0.002$	$0.23^c$
$\text{Ga}^{71}$	$\text{GaCl}_3$	$0.449 \pm 0.004$	$0.44^c$
$\text{Rb}^{85}$	$\text{RbOH}$	$0.650 \pm 0.005$	$\sim 0.6^{15}$
$\text{Rb}^{87}$	$\text{RbOH}$	$0.653 \pm 0.002$	$\sim 0.6^{15}$
$\text{Cs}^{133}$	$\text{CsCl}$	$1.49 \pm 0.01$	$\sim 1.0^{15}$

<sup>a</sup> In aqueous solution unless specified otherwise.

<sup>b</sup> In liquid  $\text{NH}_3$  solution.

<sup>c</sup> Solid.

<sup>13</sup> W. N. Tuttle, Proc. Inst. Radio Eng. 28, 23 (1940); we are indebted to T. F. Wimett for suggesting their use.

<sup>14</sup> Gutowsky, Kistiakowsky, Pake, and Purcell, J. Chem. Phys. 17, 972 (1949).

<sup>15</sup> D. F. Abell and W. D. Knight, Phys. Rev. 85, 762(A) (1952).

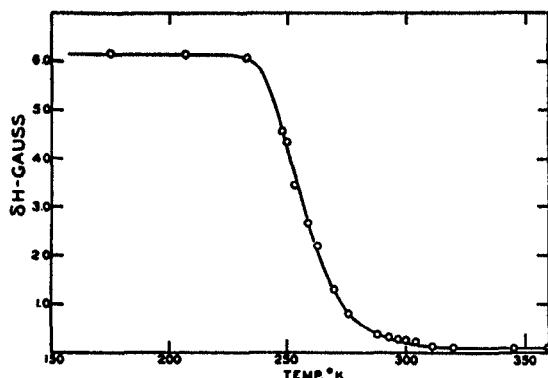


FIG. 2. The  $\text{Li}^7$  magnetic resonance line-width transition in the metal.

$\text{CuBr}$ , which was solid, and  $\text{LiNO}_3$ , which was dissolved in  $\text{NH}_3$ . Absorption intensities in the samples were adequate without the addition of paramagnetic salts,<sup>10</sup> which were not used since they introduce additional small shifts in resonance frequency.<sup>16</sup>

The resonance shifts in the metals are significant for comparison<sup>6,17</sup> with conduction electron theory. We defer discussion of this aspect of the data to a subsequent article in which our results on the temperature dependence of the resonance shifts<sup>1</sup> will be given. The present interest in the resonance shifts is their use in Eq. (1) for evaluation of  $T_1$ . It should be mentioned that there is some uncertainty in these shifts as a result of chemical shifts<sup>1,11,16</sup> among various compounds of a given element. Another source of uncertainty which we have discovered is the possibility that the resonance frequency for a salt in solution may depend on the concentration. We have observed such a dependence for  $\text{CsCl}$  and for various thallium salts. The concen-

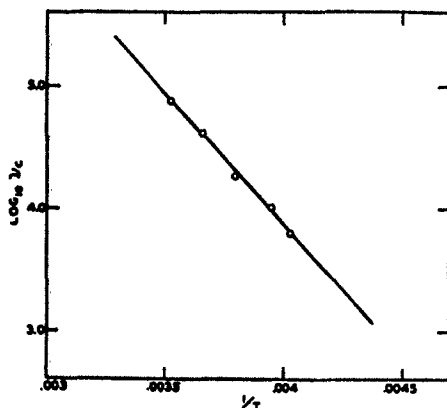


FIG. 3. The frequency  $\nu$  of diffusional motion of lithium nuclei in the metal as a function of  $1/T$ , evaluated from the line-width data. The data are fitted by the equation  $\nu = \nu_0 e^{-E_a/RT}$ , with a  $\nu_0$  value of  $2.9 \times 10^{12} \text{ sec}^{-1}$ , and  $E_a$  the activation energy for self-diffusion,  $9.8 \pm 1 \text{ kcal/mole}$ .

<sup>16</sup> W. C. Dickinson, Phys. Rev. 81, 717 (1951).

<sup>17</sup> W. Kohn and N. Bloembergen, Phys. Rev. 80, 913 (1950); Phys. Rev. 82, 283 (1951).

tration shifts are quite small for  $\text{CsCl}$  but are of the order of 0.05 percent for thallous salts in water solution. The reason for the dependence on concentration is not clear, and further work is being done in an attempt to learn its origin.

### Temperature Dependence of Line Widths

The line width has been measured as a function of temperature for  $\text{Li}^7$ ,  $\text{Na}^{23}$ ,  $\text{Rb}^{87}$ , and  $\text{Cs}^{133}$ . The behavior of the line width of lithium is similar to that observed for sodium. The measurements on sodium were reported previously.<sup>1</sup> The results for lithium are given in Fig. 2. The line width narrows with increasing temperature over a range of  $50^\circ$ , from the rigid lattice value of 6.2 gauss to about 0.1 gauss, which is due apparently to field inhomogeneity and modulation effects. This transition is centered at  $255^\circ\text{K}$ , which is  $200^\circ$  below the melting point. Such line-width transitions to narrower lines at higher temperatures are

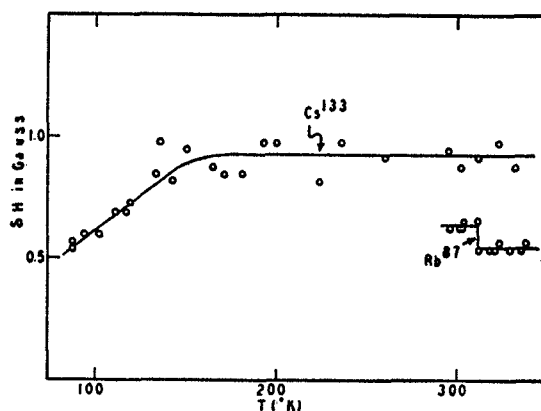


FIG. 4. The  $\text{Cs}^{133}$  and  $\text{Rb}^{87}$  magnetic resonance line widths as functions of temperature.

typical of systems in which the line width is determined by dipolar broadening.<sup>18</sup> The narrowing results from the time averaging of the dipolar fields over any nuclear motion in the sample,<sup>10</sup> and the transition in lithium, as in the case of sodium, must be attributed to self-diffusion. The frequency of motion at a given temperature can be calculated from the line-width data.<sup>18</sup> The equation  $\nu = \nu_0 e^{-E_a/RT}$  is then employed to find the activation energy  $E_a$  for the process. For lithium,  $\log_{10} \nu$  is plotted against  $1/T$  in Fig. 3, giving a value of  $9.8 \pm 1 \text{ kcal}$  for the activation energy of self-diffusion and  $2.9 \times 10^{12} \text{ sec}^{-1}$  for the frequency factor  $\nu_0$ .

The behavior of the cesium line width with temperature is given in Fig. 4. In contrast to lithium and sodium, the cesium line is broadest at higher temperatures, with a constant value of about 0.9 gauss from  $325^\circ$  to  $150^\circ\text{K}$ , and decreases linearly with temperature below  $150^\circ\text{K}$  to  $80^\circ\text{K}$ , the lowest temperature observed.

<sup>18</sup> H. S. Gutowsky and G. E. Pake, J. Chem. Phys. 18, 162 (1950).

Such a decrease in line width with temperature is inexplicable in terms of dipolar broadening. However, in Eq. (2), it is seen that the contribution of the spin-lattice interactions to the line width is proportional to  $1/T_1$ , while by Eq. (1)  $1/T_1$  is proportional to  $T$ , so if the line width is determined largely by  $T_1$ , it should be linearly proportional to the temperature. This is the case for cesium below 150°K, but at higher temperatures the line width appears to be constant. The inflection point at 150°K could be explained by assuming that the part of the line width contributed by dipolar broadening undergoes a transition due to self-diffusion as observed for lithium and sodium, but this would not account for the continued constancy at higher temperatures. The contribution to the cesium line width by dipolar interactions should be approximately 0.5 gauss in a rigid lattice. The transition in the dipolar line width must occur somewhere below the melting point since the line width does not change at the melting point. It is reasonable, therefore, to ascribe the abrupt change at 150°K in the temperature dependence of the line

TABLE II. Line widths and second moments of the resonance lines in metals.

Nucleus	Temperature	Line width $\delta H$	Second moment		$\Delta$ $\Delta H_2^2(E)$ $-\Delta H_2^2(T)$
			$\Delta H_2^2$ (Expt.)	$\Delta H_2^2$ (Theoret.)	
Li <sup>7</sup>	77°K	6.2 gauss	4.1 gauss <sup>2</sup>	4.3 gauss <sup>2</sup>	-0.2 gauss <sup>2</sup>
Na <sup>23</sup>	77	2.4	0.67	0.63	0.04
Al <sup>27</sup>	298	8.5	10.5	7.5	3.0
Al <sup>27</sup>	77	8.4	9.2	7.5	1.7
Cu <sup>63</sup>	298	6.4	6.3	5.6*	0.7
Cu <sup>65</sup>	298	5.3	5.0	4.4*	0.6
Ga <sup>69</sup>	298	0.33	...	...	...
Ga <sup>71</sup>	298	0.32	...	...	...
Rb <sup>85</sup>	313	0.50	...	0.048	...
Rb <sup>87</sup>	313	0.54	...	0.060	...
Cs <sup>133</sup>	303	0.93	...	0.077	...

\* Values in reference 1 are incorrect.

width to the transition in the dipolar contribution. Also, it should be noted that the width of the line at liquid nitrogen temperatures is approximately the same as the width due to dipolar broadening. It would be of interest to extend the line-width measurements to even lower temperatures to see if the line width again becomes constant as it should.

The line-width data for rubidium are given also in Fig. 4. The results are incomplete because it was not possible to measure the line width of Rb<sup>87</sup> at low temperatures with the present equipment. The isotopic abundance of Rb<sup>87</sup> is only 27 percent so that the signal obtained from it was rather weak. However, in the temperature range in which the line width was measured, its behavior was similar to that of cesium. The line width is essentially constant, except for a slight decrease upon warming at the melting point. Qualitatively, this decrease may be attributed to a slight increase in  $T_1$ . We have observed a small decrease in the resonance shift of Rb<sup>87</sup> at its melting point and according to Korringa's theory<sup>8</sup> this should give a small increase in  $T_1$ .

TABLE III. Inverse sixth-power internuclear distance summations for calculation of second moments of resonance lines in powders of the simpler crystal types.<sup>a</sup>

Type of lattice	$\sum_i r_{0i}^{-6}$	$\sum_i r_{0i}^{-6}$
Simple cubic	8.402a <sup>-6</sup>	...
Body centered cubic <sup>b</sup>	29.03a <sup>-6</sup>	...
Face centered cubic <sup>b</sup>	115.6a <sup>-6</sup>	...
NaCl type crystal <sup>b</sup>	115.6a <sup>-6</sup>	422.1a <sup>-6</sup>
CsCl type crystal <sup>b</sup>	8.402a <sup>-6</sup>	20.65a <sup>-6</sup>
CaF <sub>2</sub> type crystal (F)	537.7a <sup>-6</sup>	660.5a <sup>-6</sup>
CaF <sub>2</sub> type crystal (Ca)	115.6a <sup>-6</sup>	1322a <sup>-6</sup>
Hexagonal close packed	14.45b <sup>-6</sup>	...

<sup>a</sup>  $a$  is the edge of the unit cube for the cubic types;  $b$  is the side of the hexagon in the hexagonal close packed case.

<sup>b</sup> Related summations have been computed by J. E. Mayer, J. Chem. Phys. 1, 270, 327 (1933).

### Line Widths and Second Moments

The widths of the resonance lines in the metals, the experimental as well as theoretical second moments,  $\Delta H_2^2$ , and their difference  $\Delta$  are given in Table II. The theoretical second moments were calculated for nuclear magnetic dipolar broadening<sup>2</sup> from the equation for crystal powders,<sup>14</sup>

$$\Delta H_2^2 = (3/5)I(I+1)g^2\beta^2 \sum_i r_{0i}^{-6} + (4/15) \sum_i I_i(I_i+1)g_i^2\beta^2 r_{0i}^{-6}. \quad (3)$$

$g$  is here the gyromagnetic ratio of the observed nucleus, in nuclear magnetons,  $\beta$ ;  $I$  is the nuclear spin;  $r_{0i}$  the distance from a typical nucleus to its like neighbors; and the subscript  $i$  in the second term refers to unlike nuclei. The inverse sixth-power distance summations in terms of the lattice constants for the simpler crystal types are collected in Table III. The experimental lattice constants used for the various metals were taken from the Handbook of Chemistry and Physics.<sup>19</sup>

As can be seen from Table II, the experimental second moments of all the metals investigated, except lithium, are larger than the theoretical values. For lithium and sodium, the differences are within experimental error, but this is not so for Al<sup>27</sup>, Cu<sup>63</sup>, and Cu<sup>65</sup>. Also, in the case of Al<sup>27</sup>, the excess broadening  $\Delta$  is found to be dependent on the temperature. The value for  $\Delta$  at liquid nitrogen temperatures is about half of its value at room temperature. The second moments of lithium and sodium were evaluated at liquid nitrogen temperatures because of the narrowing by self-diffusion at higher temperatures. No second moments are reported for gallium because the absorption line could be picked up only in the liquid. Gallium crystallizes in a tetragonal lattice and the absorption line in the solid is presumed to be blotted out by quadrupolar effects. Experimental second moments are not reported for cesium and rubidium because the theoretical values in Table II show that the dipolar broadening should be very small for these metals. Most, if not all, of the

<sup>19</sup> Handbook of Chemistry and Physics (Chemical Rubber Publishing Company, Cleveland, 1948), 30th edition, p. 2015.

TABLE IV. The contribution of spin-lattice relaxation to the second moments of resonance lines in metals.

Nucleus	Temperature	$T_1^a$	Z	$\Delta$ (Eq. (6))	$\Delta$ (Expt.)
$\text{Li}^{27}$	77°K	$170^{22}$ gauss $^{-1}$	6 gauss	0.0002 gauss $^2$	-0.2 gauss $^2$
$\text{Na}^{23}$	77	$39^{22}$	2.7	0.004	0.04
$\text{Al}^{27}$	298	$0.41^{22}$	11	1.3	3.0
$\text{Al}^{27}$	77	$1.6^{22}$	9.5	0.3	1.7
$\text{Cu}^{63}$	298	$1.3^8$	8	0.32	0.7
$\text{Cu}^{65}$	298	$1.0^8$	7	0.35	0.6

<sup>a</sup> Extrapolated from measurements at other temperatures, assuming a linear  $1/T$  dependence.

broadening in them and also in liquid gallium appears to be due to other causes. A separate detailed discussion in terms of the line widths of these three metals is given later on.

The normalized shape function  $g(H_0 - H^*)$  for an absorption line broadened by both dipolar and spin-lattice interactions<sup>20</sup> may be written as

$$g(H_0 - H^*) = 4T_1 \int_{-\infty}^{+\infty} \frac{h(H_0' - H^*)}{1 + 16\pi^2 T_1^2 (H_0 - H_0')^2} dH_0', \quad (4)$$

where  $H_0$  is the applied magnetic field,  $H^*$  is the magnetic field at the center of the line for a given frequency,  $T_1$  is the spin-lattice relaxation time in units of gauss $^{-1}$ , and  $h(H_0 - H^*)$  is the normalized shape function determined by dipolar interactions alone. This equation is obtained by considering each energy level resulting from dipolar interactions to be broadened by the shape function

$$4T_1 [1 + 16\pi^2 T_1^2 (H_0 - H^*)^2]^{-1}, \quad (5)$$

which is just the resonance line broadened only by collisions or related phenomena.<sup>21</sup> An analysis of Eq. (4) reveals that a second moment does not exist for it even though one exists for the dipole-broadened line  $h(H_0 - H^*)$ . However, in practice, the integration is performed only over a small range of  $(H_0 - H^*)$ , so that the experimental second moments will correspond to dipolar broadening if  $T_1$  is large, for then Eq. (4) approximates  $h(H_0 - H^*)$  quite closely. For very small  $T_1$ , Eq. (4) approaches Eq. (5) as a limit, particularly if the dipolar broadening is small.

For the metals whose second moments were measured,  $T_1$  is in the range where the shape function does not approximate too closely either limiting case. Although the second moment of the shape function does not actually exist for these metals, we may consider a pseudo second moment, wherein the integration is carried out only to a finite limit as is done experimentally. For the metals considered, this pseudo second moment is, to a good approximation, the sum of the dipolar second moment and the second moment of Eq. (5) with the integration cut off at  $Z$ , where  $Z$  is

<sup>20</sup> A brief discussion is given in reference 10; for a detailed analysis see N. Bloembergen, *Nuclear Magnetic Relaxation* (Martinus Nijhoff, The Hague, 1948), p. 42.

<sup>21</sup> J. H. Van Vleck and V. F. Weisskopf, *Revs. Modern Phys.* **17**, 227 (1945).

the distance in gauss from the line center to the point at which the experimental integration terminated. Therefore, a theoretical value for  $\Delta$ , the excess broadening associated with  $T_1$ , is

$$\Delta = \left( 8T_1 Z - \frac{2}{\pi} \tan^{-1} 4\pi T_1 Z \right) / 16\pi^2 T_1^2. \quad (6)$$

Values for  $\Delta$  calculated in this way from experimental relaxation times are given in Table IV. Except for sodium, the  $T_1$  values were themselves extrapolated from observations at liquid helium temperatures.<sup>2,22</sup> The sodium value was extrapolated from experimental results<sup>23</sup> at room temperature. The extrapolations were based on the  $1/T$  dependence for  $T_1$ , predicted by Heitler and Teller<sup>7</sup> and by Korringa's theory<sup>8</sup> (Eq. (1)), which has been found to be approximately true for sodium<sup>23</sup> and aluminum.<sup>22</sup> However, at the field strengths we used,  $T_1 T$  for lithium falls off markedly at higher temperatures.<sup>22</sup> Also, the line-width temperature dependence described above for cesium indicates that  $T_1 T$  decreases for it at higher temperatures.

The calculated values of  $\Delta$  are in qualitative agreement with the experimental values. The calculated values are smaller than the experimental values for aluminum and copper, but agree with the experimental values for lithium and sodium within the experimental error. The fact that the extra broadening in aluminum should be greater than in copper is predicted as is the negligible broadening in lithium and sodium. Also the observed temperature dependence of  $\Delta$  for  $\text{Al}^{27}$  is what would be expected qualitatively from the  $1/T$  dependence of  $T_1$ . The failure of the calculated values of  $\Delta$  for aluminum and copper to agree with the experimental values is probably due to use of incorrect values of  $T_1$ . The very extensive temperature extrapolation can hardly be justified. Also, the behavior of lithium and cesium indicates that the true values of  $T_1$  at room temperature for the other metals may be smaller than the extrapolated values. For aluminum and copper a decrease in the extrapolated value of  $T_1$  by a factor of about  $\frac{1}{2}$  will give values of  $\Delta$  in agreement with the experimental broadening. One can also estimate  $T_1$  values from the resonance shifts in Table I. These  $T_1$  values agree only approximately with the  $T_1$  values obtained by the temperature extrapolation and result in  $\Delta$  values in poorer agreement with experiment.

Further evidence that the broadening is due to the spin-lattice interaction is furnished by the absorption lines of rubidium, cesium, and gallium. The lines for these metals in the liquid state are considerably broader than the 0.05 to 0.1 gauss modulation and inhomogeneity broadening, and the widths do not change appreciably upon going between the liquid and solid states. Also, the lines in these metals are definitely Lorentzian in shape as can be seen in Fig. 5, where

<sup>22</sup> N. J. Poulis, *Physica* **16**, 373 (1950).

<sup>23</sup> R. E. Norberg and C. P. Slichter, *Phys. Rev.* **83**, 1074 (1951).



the cesium derivative curve is plotted along with the derivative of a Lorentzian line with the same line width and passing through one point on the experimental curve. The fact that these absorption lines are Lorentzian in shape is experimental justification of our use of Eq. (5) as the broadening function and confirms our postulate that spin-lattice relaxation determines the width of the lines. Applying Eq. (5) to these three metals, we may compute  $T_1$  from the experimental line widths by use of the subsequent equation,

$$T_1 = 1/2\pi\sqrt{3}\delta H, \quad (7)$$

where  $T_1$  will be given in units of gauss<sup>-1</sup> if  $\delta H$  is in gauss.

Values of  $T_1$  computed by this equation from the experimental line widths are given in Table V. Aside from the assumption of the validity of Eq. (5), there is the error introduced by the 0.05 to 0.1 gauss contributed to the line widths by modulation effects and field inhomogeneity. An estimated average correction of 0.07 gauss has been subtracted from the experimental line widths, increasing the  $T_1$  values by up to 25 percent.

TABLE V. A comparison of  $T_1$  values from line widths with those from the resonance shifts.

Nucleus	Temperature	Corrected <sup>a</sup> $\delta H$	$T_1$ from $\delta H$ (Eq. (7))	$T_1$ from $\Delta H/H$ (Eq. (1))
Ga <sup>69</sup>	298°K	0.26 gauss	$0.34 \times 10^{-3}$ sec	$0.75 \times 10^{-3}$ sec
Ga <sup>71</sup>	298	0.25	0.28	0.47
Rb <sup>85</sup>	313	0.43	0.52	2.2
Rb <sup>87</sup>	313	0.47	0.14	0.19
Cs <sup>133</sup>	303	0.86	0.19	0.23

<sup>a</sup> Values from Table II less an estimated average 0.07 gauss broadening from field inhomogeneity and modulation effects.

Experimental spin-lattice relaxation times have not been reported so our values computed from the line widths by Eq. (7) can be compared only with those obtained with Eq. (1) from the resonance shifts. These values of  $T_1$ , computed from the experimental resonance shifts in Table I, are given in Table V for comparison. The agreement between the two sets of values is perhaps better than might be expected in view of the approximations in Korringa's theory.<sup>8</sup> The resonance

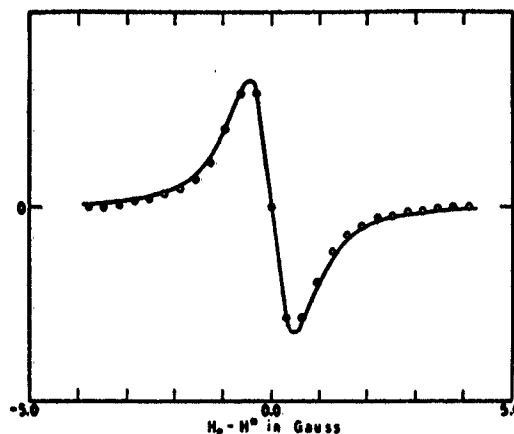


FIG. 5. The derivative of the Cs<sup>133</sup> magnetic resonance line at room temperature compared to a Lorentzian line shape. The circles are experimental data; the line represents the derivative of a Lorentzian curve with the same line width and adjusted to pass through one of the experimental points.

shift  $T_1$  values are consistently higher than those from line broadening, the factor being a maximum of two for Ga<sup>69</sup>. One particular deviation is found in the  $T_1$  values for different isotopes of the same metal. Equation (1) predicts that the ratio of relaxation times for two isotopes should equal the square of the inverse ratio of their  $g$  values. However, the line-width data on the isotopes of both rubidium and gallium give ratios of relaxation times equal to somewhat less than the second power of the inverse ratio of the  $g$  values.

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## Nuclear Magnetic Resonance Multiplets in Liquids\*

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Multiple magnetic resonance lines have been observed for  $H^1$ ,  $F^{19}$ , and  $P^{31}$  nuclei in compounds such as  $PH_3$ ,  $PF_3$ ,  $F_2PO(OH)$ , and  $BrF_3$ , in the liquid state. The multiplets consisted of two to seven equally spaced narrow components, symmetrically placed about a central frequency, and with splittings from 0.02 to 0.8 gauss. These multiplets arise from a new variety of interaction among the nuclear moments in a molecule. Resonance lines were found to be multiple either when a nucleus interacted with a different species of nucleus or when there was interaction between nuclei of the same species with resonance frequencies separated by a chemical shift. No compounds exhibited multiplets attributable to interactions among structurally equivalent nuclei. Nor were multiplets caused by nuclei whose electric quadrupole moments were coupled to a direction fixed in the molecule.

The number and relative intensities of the components of a multiplet were determined by the number and statistical weights of the various nuclear spin orientations of the nuclei causing the splitting. In a given molecule, the ratio of the multiplet splittings of the two different resonance lines was inversely proportional to the ratio of the gyromagnetic ratios of the interacting nuclei. The splittings were independent of applied magnetic field at 4180

and 6365 gauss; they were independent of temperature over ranges from 55°C to -130°C. In  $PF_3$ , the one gas examined, the splitting of the doublet fluorine resonance was the same in the gas and liquid phases; also, the doublet was demonstrated to arise from coupling with the phosphorus nucleus, rather than from a chemical shift between the resonances from the apex and meridian fluorines in the bipyramidal structure, as proposed earlier.

All of the above characteristics are accounted for theoretically by assuming the magnetic nuclei interact via magnetic fields inside the molecule. The qualitative aspects are predicted by coupling of the form  $A_{12} \mathbf{u}_1 \cdot \mathbf{u}_2$  between the nuclear moments  $\mathbf{u}_1$  and  $\mathbf{u}_2$ . The coupling constant  $A_{12}$  depends upon the detailed mechanism, which must involve the molecular electrons. Second-order perturbation theory was used to calculate the relative magnitudes of coupling via the electron orbital and the electron spin magnetic moments. The electron spin mechanism was found to give splittings ten to twenty times the orbital. Approximate calculation of the electron spin mechanism in several simpler cases gave good agreement with experiment. The influence upon the splittings of electric quadrupole coupling and spin-lattice relaxation was considered and is discussed briefly.

### INTRODUCTION

In earlier observations of nuclear magnetic resonance,<sup>1</sup> the absorption lines in liquids were found to be single. This agreed with the fact that the direct magnetic interaction between two nuclear spins would average to zero over all the orientations possible in the liquid state.<sup>2</sup> The width of the resultant single, narrow resonance line is determined usually by inhomogeneities in the applied magnetic field<sup>3</sup> or else by the relaxation processes.<sup>3</sup> If the nuclear spin is greater than  $\frac{1}{2}$ , an electric quadrupole moment exists and can interact with electric field gradients at the nucleus; however, the resultant splitting of the resonance line in single crystals<sup>4</sup> is averaged also in the liquid state to a more or less broadened single line.

The discovery of chemical shifts<sup>5</sup> in the magnetic shielding of nuclei led to the observation<sup>6,7</sup> of complex resonance lines in liquids with structurally nonequiva-

lent nuclei of the given species. In such cases, the number and relative intensities of the component lines are given usually<sup>8</sup> by the number and population of nonequivalent sets of the nucleus observed. For example, the fluorine resonance in liquid *para*-fluorobenzotrifluoride,  $CF_3-C_6H_4-F$ , has two narrow components with an intensity ratio of 3 to 1. The separation of the components is directly proportional<sup>9</sup> to the applied magnetic field because the nuclear magnetic shielding results from the interaction between the applied field and the molecular electrons. The relative magnitudes of the chemical shifts are determined by the differences in electron distribution about the nuclei.

In this paper, the principle concern is another new type of complex resonance line in liquids. The fluorine resonance in  $PF_3$  was found<sup>10</sup> to be a doublet, with narrow components of equal intensity separated by 0.35 gauss. The structural equivalence of the fluorines and the preparation and purification of samples by different methods eliminated chemical shifts and impurities as possible causes of the doublet. Similar multiple fluorine and phosphorus resonance lines<sup>11</sup> were observed later in  $POCl_2F$ ,  $POClF_2$ , and  $CH_3OPF_2$ , the

\* Supported in part by the ONR.

<sup>1</sup> Purcell, Torrey, and Pound, *Phys. Rev.* **69**, 37 (1946); Bloch, Hansen, and Packard, *Phys. Rev.* **69**, 127 (1946). See also G. E. Pake, *Am. J. Phys.* **18**, 438, 473 (1950) for a general review and bibliography.

<sup>2</sup> Bloembergen, Purcell, and Pound, *Phys. Rev.* **71**, 466 (1947).

<sup>3</sup> R. M. Brown, *Phys. Rev.* **78**, 530 (1950).

<sup>4</sup> R. V. Pound, *Phys. Rev.* **79**, 685 (1950).

<sup>5</sup> W. D. Knight, *Phys. Rev.* **76**, 1259 (1949); W. C. Dickinson, *Phys. Rev.* **77**, 736 (1950); W. G. Proctor and F. C. Yu, *Phys. Rev.* **77**, 717 (1950).

<sup>6</sup> H. S. Gutowsky and C. J. Hoffman, *Phys. Rev.* **80**, 110 (1950).

<sup>7</sup> E. L. Hahn, *Phys. Rev.* **80**, 580 (1950).

<sup>8</sup> Gutowsky, McCall, McGarvey, and Meyer, *J. Am. Chem. Soc.*, **74**, 4809 (1952).

<sup>9</sup> N. F. Ramsey, *Phys. Rev.* **78**, 699 (1950).

<sup>10</sup> Gutowsky, Hoffman, and McClure, *Phys. Rev.* **81**, 305(A) (1951).

<sup>11</sup> H. S. Gutowsky and D. W. McCall, *Phys. Rev.* **82**, 748 (1951).



Fig. 1. Oscilloscope photograph of the doublet fluorine magnetic resonance in  $\text{POCl}_3\text{F}$ , using a slow-sweep modulation of the applied magnetic field. The applied field is about 6365 gauss; the modulation about 0.8 gauss; and the splitting is 0.294 gauss.

details of which suggested magnetic interaction between the fluorine and phosphorus nuclei. Since then, other examples have been found, and investigations made of the influence upon the multiplets of factors such as temperature, applied magnetic field, nuclear species, and molecular structure. A brief general account of the results has been published elsewhere,<sup>12</sup> with the proposal that the multiplets arise from an indirect magnetic interaction of the nuclei by a second-order process involving the molecular electrons. Herein are presented the details of the experiments and the theoretical analysis.

Several other results related to this discussion have been published. Proctor and Yu<sup>13</sup> reported the  $\text{Sb}^{121}$  and  $\text{Sb}^{123}$  resonances in an aqueous HF solution of  $\text{NaSbF}_6$  to be symmetrical multiplets, with splittings of 1.90 gauss, and at least five, probably seven, and perhaps nine components, with intensities decreasing from the central line. A qualitative interpretation<sup>13</sup> on the basis of rotational hindrance was extended in detail by Andrew<sup>14</sup> who suggested hydrogen bonding could constrain the octahedral  $\text{SbF}_6^-$  ion to rotate about a tetrad axis. In this event, the direct magnetic interactions between the antimony and fluorine nuclei would not average to zero and a symmetrical fine structure is predicted similar to that observed in rigid lattice solids<sup>15</sup> or in several cases of restricted rotation in solids.<sup>16</sup> Andrew's ingenious analysis is in good agreement with Proctor and Yu's initial observations; however, rotational hindrance is unable to account for the multiplets<sup>12</sup> observed in the other compounds. Recently, Dharmatti<sup>17</sup> and Weaver re-examined the  $\text{SbF}_6^-$  case experimentally in detail, and showed it to be similar in nature to the multiplets observed here. They found seven components in the antimony resonances with intensities going as the binomial coefficients, in accord with the rules<sup>11,12</sup> for the multiplets.

<sup>12</sup> Gutowsky, McCall, and Slichter, *Phys. Rev.* **84**, 589 (1951).

<sup>13</sup> W. G. Proctor and F. C. Yu, *Phys. Rev.* **81**, 20 (1951).

<sup>14</sup> E. R. Andrew, *Phys. Rev.* **82**, 443 (1951).

<sup>15</sup> G. E. Pake, *J. Chem. Phys.* **16**, 327 (1948).

<sup>16</sup> H. S. Gutowsky and G. E. Pake, *J. Chem. Phys.* **18**, 162 (1950).

<sup>17</sup> S. S. Dharmatti, and H. E. Weaver, Jr., *Phys. Rev.* **87**, 675 (1952). We are grateful to them for sending us their results prior to publication.

It often happens that two independent and apparently different lines of research are found to be related. The steady-state multiplet studies reported here and the "slow-beat" effects<sup>7</sup> in spin echoes are an interesting example. Much parallel work was done by Hahn and Maxwell<sup>18</sup> at Stanford and by these laboratories before it became clear that both groups were dealing with the same physical phenomena. The parallel was obscured by large differences in the types of compounds and the magnitudes of the effects observed by the two groups. In our case, a combination of chemical shifts and small multiplet splitting was observed<sup>19</sup> in the fluorine resonances of  $\text{BrF}_3$  and  $\text{IF}_3$ , and later it was found<sup>20</sup> that these compounds exhibited the "slow-beat" spin-echo effects. On the other hand, Hahn discovered the "slow-beats" in the proton spin echoes of ethanol,<sup>7</sup> and later the steady state resonance was resolved<sup>21</sup> into a combination of chemical shifts and multiplet splittings similar to those in  $\text{BrF}_3$  and  $\text{IF}_3$ , but much smaller. The phenomena found with the different methods and compounds appear to arise from the same cause; however, the theoretical analyses and the observables are quite different in the two experiments. Many of the conclusions reported in this paper concerning the nature of the nuclear interactions have been reached independently by Hahn and Maxwell.<sup>18</sup> Although there has been considerable duplication of thinking, we feel that the independent and originally unrelated approaches have led to a deeper understanding of the phenomena. It is a pleasure to acknowledge several interesting exchanges of information with the Stanford group.

## EXPERIMENTAL

Most of the equipment and procedures have been described in detail previously.<sup>19</sup> The resonance lines were displayed on an oscilloscope, using 30 cycle per second modulation<sup>2</sup> of the applied magnetic field, or else a slow-sweep saw-tooth<sup>19,21</sup> at about one cycle per second. The choice of modulation depended on the splittings, interference between the relaxation wiggles,<sup>2</sup> and line widths. Chemical shifts and multiplet splittings were observed as differences in the applied magnetic field at a fixed resonance frequency. The chemical shifts are defined as  $(H_r - H_c)/H_c$ , where  $H_r$  and  $H_c$  are the fields applied for the resonance in the reference and for the center of any multiplet line structure in the compound; the differences were found by interchanging the sample and reference. Trifluoroacetic acid,  $\text{CF}_3\text{CO}_2\text{H}$ , was used as the reference<sup>22</sup> for the fluorine shifts, aque-

<sup>18</sup> E. L. Hahn and D. E. Maxwell, *Phys. Rev.* **84**, 1246 (1951).

<sup>19</sup> H. S. Gutowsky and C. J. Hoffman, *J. Chem. Phys.* **19**, 1259 (1951).

<sup>20</sup> McNeil, Slichter, and Gutowsky, *Phys. Rev.* **84**, 1245 (1951).

<sup>21</sup> M. E. Packard and J. T. Arnold, *Phys. Rev.* **83**, 210(A) (1951); Arnold, Dharmatti, and Packard, *J. Chem. Phys.* **19**, 507 (1951).

<sup>22</sup> The chemical shifts given here can be converted to the  $F_2$  scale used in reference 19 by adding  $50.76 \times 10^{-3}$ , which is the chemical shift of trifluoroacetic acid on the  $F_2$  scale.

ous phosphoric acid for phosphorus, while the hydrogen data have been reduced to the unshielded proton.<sup>19</sup> In most cases, a series of ten measurements was made giving probable statistical errors, for the splittings, of about  $\pm 0.001$ ,  $\pm 0.002$ , and  $\pm 0.003$  gauss for the  $H^1$ ,  $F^{19}$ , and  $P^{31}$  resonances, respectively, and about twice as much for the chemical shifts and for lower fields. In addition, there are possible systematic errors of  $\pm 1.0$  percent of the measured values.<sup>19</sup>

The effect of applied magnetic field was investigated by using permanent magnets of 4180 and 6365 gauss. The design and operation of the smaller magnet is generally similar to that of the larger.<sup>19</sup> Earlier field dependence observations<sup>12</sup> were made with the assistance of T. R. Carver, using an electromagnet. A cryostat<sup>19</sup> was used to investigate the influence of temperature on the splittings and also to condense  $PH_3$ ,  $PF_3$ ,  $PF_5$ , and  $POF_3$  to the liquids for observation at about  $-90^\circ C$ . Otherwise, most experiments were on the liquids or aqueous solutions at room temperature. The higher boiling compounds were sealed in Pyrex, polyethylene, or Kel-F polymer<sup>20</sup> tubes.

The samples of  $PH_3$ ,  $PF_3$ , and  $PF_5$  were synthesized, and purified by bulb to bulb distillation. The  $POF_3$  was formed by the moisture catalyzed reaction of  $PF_5$  with the  $SiO_2$  in Pyrex.<sup>24</sup> The fluorine resonance from the  $SiF_4$  also produced in the reaction was identified from its chemical shift observed previously<sup>19</sup> in the pure compound. The  $BrF_3$  and  $IF_5$  were commercial samples from Harshaw Chemical Company; the  $PBr_3$  from Dow Chemical Company; the  $PCl_3$ ,  $P_4(y)$ , and  $H_2SiF_6$  from J. T. Baker and Company; the  $NH_4ZrF_6$  from Delta Chemical Company; and the  $HFBr_4$  from General Chemical Division. The inorganic fluosilicates were obtained from Dr. Glenn C. Finger of the Illinois State Geological Survey. The  $CH_3OPF_2$ ,  $POCl_2F$ ,  $POClF_2$ ,  $PSCl_3$ ,  $POCl_3$ ,  $PI_3$ , and  $P_2I_4$  were supplied by Dr. D. R. Martin, then at this university. The K-25 laboratories of Carbide and Carbon Chemicals Division at Oak Ridge furnished the  $MoF_6$ ,  $WF_6$ , and  $UF_6$ . The phosphorous acid,  $HPO(OH)_2$  (70 percent), and hypophosphorous acid,  $H_2PO(OH)$  (50 percent), were donated by the Oldbury Electrochemical Company. Samples of  $FPO(OH)_2$ ,  $F_2PO(OH)$ ,  $HPF_6$  (65 percent),  $KPF_6$ ,  $Na_2PO_3F$ , and  $NH_4VF_6$  were donated by Dr. Wayne E. White of Ozark-Mahoning Company.

## RESULTS AND DISCUSSION

### The Fluorine Magnetic Resonance

#### Phosphorus Compounds

Figure 1 is an oscilloscope photograph of the doublet fluorine resonance in  $POCl_2F$ , at an applied magnetic field of 6365 gauss; this resonance is typical of the

fluorine doublets observed in the eleven fluorine containing phosphorus compounds investigated. The total field sweep in the picture is 0.8 gauss; the splitting is 0.294 gauss. It is seen that the components are of equal intensity and narrow compared to the splitting; in fact, the widths of the components were determined by inhomogeneities in the applied field, which were about 0.03 gauss over the sample volume used in this case. Table I summarizes the splittings and chemical shifts. In  $HPF_6$  several weak lines were found besides the strong doublet given in Table I; the weak lines occurred at applied fields corresponding to  $F_2PO(OH)$ ,  $FPO(OH)_2$ , and  $SiF_6^{2-}$ , with an unassigned single line at a chemical shift of  $6.90 \times 10^{-5}$ . In the samples of  $F_2PO(OH)$  and  $FPO(OH)_2$  weak lines were obtained from the hydrolysis products.

The fluorine resonance in  $PF_5$  was reported earlier to be a doublet with components of unequal intensity interpreted<sup>19</sup> as arising from a chemical shift between the apex and meridian plane fluorines in the trigonal bipyramid structure. However, the subsequent observation of fluorine doublets in all other compounds with only structurally identical fluorines bound to phosphorus called for a re-investigation of  $PF_5$ . No additional fine structure was found in the two components, with resolution at least 0.03 gauss. Moreover, the two components were found<sup>25</sup> to be of equal intensity within an experimental error of less than  $\pm 3$  percent, upon observation with a sensitive spectrometer, narrow-band amplifier, and recording potentiometer. Finally, the splitting was found to be the same at 4180 and 6365 gauss, eliminating conclusively the field-dependent<sup>5,9</sup> chemical shift. The absence of even a small chemical shift suggests that the electron distribution must be very nearly the same about the structurally distinguishable apex and meridian fluorines in  $PF_5$ , at least when averaged over the lifetime of the nuclear magnetic states.

TABLE I. The fluorine multiplets and chemical shifts in several phosphorus compounds.<sup>a</sup>

Compound	Line structure <sup>b</sup>	Splitting	Chemical shifts <sup>c</sup>
$PF_5$	(1-1)	0.350 gauss	$-4.34 \times 10^{-5}$
$CH_3OPF_2$	(1-1)	0.320	-2.50
$POCl_2F$	(1-1)	0.294	-6.90
$POClF_2$	(1-1)	0.280	-3.04
$POF_3$	(1-1)	0.264	+1.58
$F_2PO(OH)$	(1-1)	0.244	+0.90
$FPO(OH)_2$	(1-1)	0.238	-0.25
$PF_5$	(1-1)	0.232	-0.50
$Na_2PO_3F$ (aq.)	(1-1)	0.195	+2.68
$HPF_6$	(1-1)	0.178	-0.55
$KPF_6$ (aq.)	(1-1)	0.176	-0.77

<sup>a</sup> Measurements were made at an applied field of 6365 gauss.

<sup>b</sup> The numbers are the relative intensities of the components observed in the resonance for each compound.

<sup>c</sup> Referred to  $CF_3CO_2H$ .

<sup>20</sup> Available from Plax Corporation, Hartford, Connecticut. Threaded joints were sealed with a fluorocarbon polymer wax.

<sup>24</sup> A. B. Burg, "Volatile Inorganic Fluorides" in *Fluorine Chemistry* (Academic Press, Inc., New York, 1950), p. 98.

<sup>25</sup> These observations were made on the gas in a sealed tube at room temperature at a pressure of five atmospheres.

TABLE II. The fluorine multiplets and chemical shifts in  $\text{BrF}_3$  and  $\text{IF}_3$  at different magnetic fields.

Compound and line structure <sup>a</sup>	Splitting		External <sup>b</sup>	Chemical shifts Internal <sup>a</sup>		R
	at 6365 gauss	at 4180 gauss		at 6365 gauss	at 4180 gauss	
$\text{BrF}_3$	gauss	gauss		gauss	gauss	
(a) (32-32)	0.019	0.020	$-21.71 \times 10^{-3}$	0.876	0.576	1.521
(b) (1-4-6-4-1)	0.019		-35.47			
$\text{IF}_3$						
(a) (32-32)	0.021	0.021	-8.94	0.314	0.205	1.531
(b) (1-4-6-4-1)	0.021		-13.87			

<sup>a</sup> (a) and (b) are chemically shifted components; numbers are relative intensities of various components observed in the resonance for each compound.

<sup>b</sup> Referred to  $\text{CF}_3\text{CO}_2\text{H}$ ; values taken from reference 19.

<sup>c</sup> These values are the separations in gauss of the chemically shifted sets of multiplets. R, the ratio of the internal shifts, should equal 1.523, the ratio of the applied fields.

### $\text{BrF}_3$ and $\text{IF}_3$

The fluorine resonance in each of these compounds was complex, consisting of two multiplets with the same small splittings of about 0.02 gauss, the stronger one a doublet and the weaker a quintuplet. The data in Table II show the splittings to be field independent, while in each case the separation in gauss between the two multiplets was proportional to the field and thus a chemical shift. This confirms the assignment<sup>19</sup> of the stronger multiplet to the four coplanar fluorines and the weaker multiplet to the apex fluorine in a tetragonal pyramid molecule. It is only in compounds such as these, with a combination of chemical shifts and multiplets for a given resonance, that the "slow beats" have been observed<sup>7,18,20</sup> in the spin-echo experiments.<sup>26</sup>

### Other Fluorides

The fluorine resonances were examined in a number of other compounds with structures pertinent to the origin of the multiplets. Single sharp lines were found in liquid  $\text{MoF}_6$ ,  $\text{WF}_6$ , and  $\text{UF}_6$  as well as in aqueous solutions of a number of fluosilicate salts,  $\text{MSiF}_6$  ( $\text{M} = \text{Cu}, \text{Mg}, \text{Co}, \text{and Zn}$ ), and also of  $\text{NH}_4\text{ZrF}_6$ . In these compounds the central atoms, to which the fluorines are bound, have zero or very small magnetic moments, at least in the case of isotopes present in appreciable abundance. Moreover, the molecules and ions have octahedral or very nearly octahedral<sup>27</sup> symmetry, with equivalent or essentially equivalent fluorines. So in these compounds there should be neither multiplet splitting nor chemically shifted components, in agreement with observations.

Aqueous  $\text{H}_2\text{SiF}_6$  is similar to the HF solution of

<sup>28</sup> The "slow beats" have not been found in compounds such as  $\text{POCl}_3$  where the multiplet splitting results from interaction between different nuclear species. In these compounds an rf pulse at say the fluorine resonance frequency would leave the phosphorus nuclei virtually unaffected. Hence the phosphorus spin would merely act like a magnetic field inhomogeneity in shifting the resonance, and would not affect the echo.

<sup>27</sup> This applies to  $\text{MoF}_6$ ,  $\text{WF}_6$ , and  $\text{UF}_6$ ; Burke, Smith, and Nielsen, J. Chem. Phys. 20, 447 (1952).

$\text{NaSbF}_6$  in which Proctor and Yu<sup>18</sup> found the antimony multiplets. Extensive hydrogen bonding or lack of dissociation of the  $\text{H}_2\text{SiF}_6$  was indicated by the observation of two proton resonances of unequal intensity in the solution, one probably from the  $\text{H}_2\text{O}$  and the other from protons bound to  $\text{SiF}_6^-$ . Thus the restricted rotation mechanism of Andrew<sup>14</sup> might be expected to give a complex or broadened fluorine resonance; on the other hand,  $\text{Si}^{28}$  has a zero magnetic moment so there could be no multiplet type splitting. Actually, a single sharp fluorine resonance was found, confirming the conclusion of Dharmatti and Weaver<sup>17</sup> that the antimony multiplets do not arise from restricted rotation.

Multiplets might be expected in aqueous  $\text{NH}_4\text{VF}_6$  and  $\text{HBF}_4$ , since  $\text{B}^{11}$  and  $\text{V}^{51}$  have relatively large magnetic moments and are present in high abundance. However, only somewhat broadened resonance lines were found. In  $\text{HBF}_4$ , the widths of the proton and fluorine resonances appeared to be determined by field inhomogeneities of about 0.01 gauss, with the  $\text{B}^{11}$  resonance slightly but definitely broader, about 0.02 gauss. In the  $\text{NH}_4\text{VF}_6$  solution, the fluorine resonance was broadened to about 0.05 gauss, while the  $\text{V}^{51}$  resonance was about 0.15 gauss.

### The Proton Magnetic Resonance

Multiple proton lines were observed in the three phosphorus containing compounds  $\text{PH}_3$ ,  $\text{H}_2\text{PO}(\text{OH})$ , and  $\text{HPO}(\text{OH})_2$ . In  $\text{PH}_3$  the proton resonance was a doublet but with a much smaller splitting than that of the fluorine in  $\text{PF}_3$ . The proton resonances in both  $\text{H}_2\text{PO}(\text{OH})$  and  $\text{HPO}(\text{OH})_2$  were complex, with a partially resolved line displaced by several milligauss from the mid-point of a rather weak doublet. The central line is assigned to the protons in the water and in the OH groups attached to phosphorus, and the doublet to the protons bound directly to the phosphorus. The splittings and chemical shifts of the doublets are given in Table III.

### The Phosphorus Magnetic Resonance

In contrast to the fluorine and hydrogen doublet resonances observed in the phosphorus compounds, the phosphorus resonances in the same compounds had

TABLE III. The proton multiplets and chemical shifts in some phosphorus compounds.<sup>a</sup>

Compound	Line structure <sup>b</sup>	Splitting	Chemical shifts <sup>c</sup>
$\text{PH}_3$ <sup>d</sup>	(1-1)	0.043 gauss	$2.93 \times 10^{-3}$
$\text{HPO}(\text{OH})_2$	(1-1)	0.166	2.83
$\text{H}_2\text{PO}(\text{OH})$	(1-1)	0.137	2.64

<sup>a</sup> Measurements were made at an applied field of 6365 gauss.

<sup>b</sup> The numbers are the relative intensities of the components observed in the resonance for each compound.

<sup>c</sup> Referred to the unshielded proton.

<sup>d</sup> The chemical shift for  $\text{PH}_3$  agrees with the trends reported in reference 19 for other hydrides.

from two to seven components. In these multiplets, as well as all others observed, the number of components was  $(2M_I + 1)$ , where  $M_I$  is the maximum value of the total nuclear spin quantum number of the nuclei responsible for the splitting. The relative intensities of the components agreed with the statistical weights of the associated  $M_I$  values, the weights being given ordinarily by the binomial coefficients.

Figure 2 is an oscilloscope photograph of the triplet phosphorus resonance in  $\text{CH}_3\text{OPF}_2$ . Similar triplets were observed in  $\text{POCl}_2\text{F}$ ,  $\text{F}_2\text{PO}(\text{OH})$ , and  $\text{H}_2\text{PO}(\text{OH})$ . The total range in applied field in Fig. 2 is 2.0 gauss; the observed splitting is 0.740 gauss. It is seen that the components have relative intensities of 1:2:1 and are very narrow in comparison to their separation. The line widths, as in the case of the proton and fluorine multiplets, were determined usually by field inhomogeneities. In the  $\text{FPO}(\text{OH})_2$  sample the phosphorus resonance was partially obscured by the presence of  $\text{H}_3\text{PO}_4$  and  $\text{F}_2\text{PO}(\text{OH})$ ; in addition the doublet components may have been somewhat broader than field inhomogeneities. In any event, no good phosphorus measurements could be obtained on it nor on the  $\text{PF}_5$ ,  $\text{POF}_3$ , aqueous  $\text{KPF}_6$ , and  $\text{Na}_2\text{PO}_3\text{F}$  samples in which the resonances were too weak for accurate measurement. The line structures, splittings, and chemical shifts found in the other nine compounds are given in Table IV.

Single phosphorus resonance lines were observed in several compounds where the only other magnetic nuclei attached directly to phosphorus have electric quadrupole moments. These include  $\text{PCl}_3$ ,  $\text{PBr}_3$ ,  $\text{PI}_3$ ,  $\text{POCl}_3$ , and  $\text{PSCl}_3$ . Single lines were found also in yellow phosphorus ( $\text{P}_4$ ) and in  $\text{I}_2\text{P}-\text{PI}_2$  in both of which the phosphorus nuclei are in structurally equivalent positions.

#### Temperature Experiments

The influence of temperature on the splittings was checked for the fluorine resonances in  $\text{CH}_3\text{OPF}_2$  and  $\text{HPF}_6$ , and for the fluorine and phosphorus resonances in  $\text{POCl}_2\text{F}$ . In all cases, the splittings were independent of temperature, within experimental error, over the observed range. Observations on  $\text{POCl}_2\text{F}$  extended from

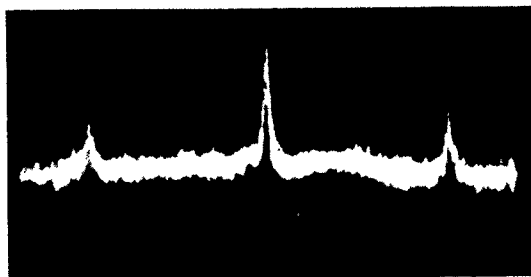


FIG. 2. Oscilloscope photograph of the triplet phosphorus magnetic resonance in  $\text{CH}_3\text{OPF}_2$ , using a slow-sweep modulation of the applied magnetic field. The applied field is about 6365 gauss, the modulation about 2.0 gauss; and the splitting is 0.740 gauss.

TABLE IV. The phosphorus multiplets and chemical shifts in some compounds with fluorine or hydrogen.\*

Compound	Line structure†	Splitting	Chemical shift‡
$\text{PF}_5$	(1-3-3-1)	0.818 gauss	$-9.7 \times 10^{-3}$
$\text{CH}_3\text{OPF}_2$	(1-2-1)	0.740	-11.1
$\text{POCl}_2\text{F}$	(1-1)	0.684	0.0
$\text{POClF}_2$	(1-2-1)	0.659	+1.5
$\text{F}_2\text{PO}(\text{OH})$	(1-2-1)	0.570	+2.1
$\text{HPF}_6$	(1-6-15-20-15-6-1)§	0.41	+14.8
$\text{HPO}(\text{OH})_2$	(1-1)	0.410	-0.4
$\text{H}_2\text{PO}(\text{OH})$	(1-2-1)	0.344	-1.4
$\text{PH}_3$	(1-3-3-1)	0.104	+24.1

\* Measurements were made at an applied field of 6365 gauss.

† The numbers are the relative intensities of the components observed in the resonance for each compound.

‡ Referred to aqueous phosphoric acid,  $\text{H}_3\text{PO}_4$ .

§ Resonance too weak for oscilloscope display; intensities estimated from output of narrow-band amplifier.

55°C to -90°C, and on  $\text{CH}_3\text{OPF}_2$  and  $\text{HPF}_6$  from room temperature to -130°C and -80°C, respectively. Experimental error was  $\pm 0.01$  gauss for the phosphorus resonance in  $\text{POCl}_2\text{F}$  and  $\pm 0.003$  gauss for the fluorine resonances in the three compounds. At the lower temperatures the intensities of the multiplet lines decreased as a broad-line background developed; however, the splittings remained constant as the sharp components disappeared into the broad line resulting from the freezing out of the molecular reorientations.<sup>2,16</sup> The fluorine splittings in  $\text{PF}_5$  were observed in the liquid phase<sup>19</sup> at -75°C and in the gas at five atmospheres at room temperature.<sup>20</sup> The change in state did not change the splittings, demonstrating conclusively that restricted rotation in the liquid phase is not the origin of the splittings, at least in  $\text{PF}_5$ .

#### Different Applied Magnetic Fields

Proctor and Yu<sup>13</sup> found the splittings of the  $\text{Sb}^{121}$  and  $\text{Sb}^{123}$  resonances in aqueous  $\text{NaSbF}_6$  to be independent of applied magnetic field. Also, indirect confirmation of the field independence of the multiplet splittings has been provided in several cases<sup>7,18,20</sup> by the related "slow-beats" in spin echo experiments. In addition, we have made a number of direct measurements of the  $\text{H}^1$ ,  $\text{F}^{19}$ , and  $\text{P}^{31}$  splittings in several compounds at applied fields of 4180 and 6365 gauss. It is seen from the results summarized in Table V that the splittings are field independent. Similar data have been given above in Table II for  $\text{BrF}_5$  and  $\text{IF}_5$ , in which the fluorine chemical shifts are directly proportional to the applied field while the splittings are field independent.

#### Relation of Splittings to Nuclear Magnetic Moments

The nuclear origin of the splittings is demonstrated by the interdependence of the splittings and the magnetic moments of the different nuclear species in the same molecules.<sup>11</sup> Table VI lists the ratios of the splittings observed for two different resonance lines in

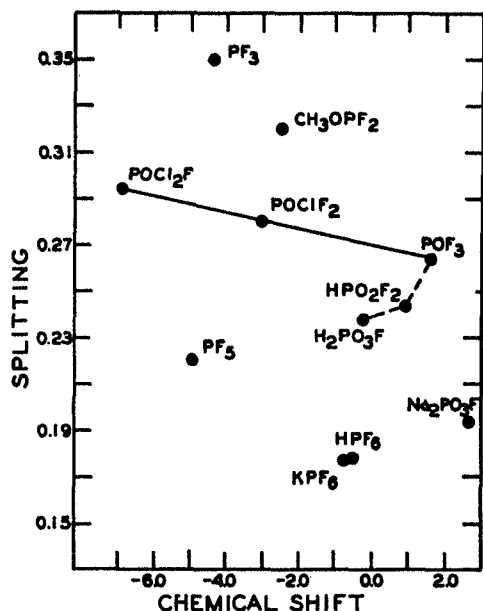


FIG. 3. The multiplet splittings in gauss, of the fluorine magnetic resonance plotted against the chemical shifts, in units of  $10^4 \times (H_e - H_r)/H_r$ , where  $H_e$  and  $H_r$  are the applied fields required for resonance in the compound and in the  $\text{CH}_3\text{CO}_2\text{H}$  reference, respectively. The data were obtained at 6365 gauss.

several compounds. It is seen that  $(\delta H_A/\delta H_B) = \mu_B/\mu_A$ , within experimental error, where  $\delta H$  is the splitting and  $\mu$  the magnetic moment of the nucleus. Strictly speaking, this rule holds only for nuclei of the same spin; the general relation is given in the theoretical discussion.

### General Results and Conclusions

The existence and size of multiplet splitting in a particular resonance depends upon several factors. Splittings have *not* been found which can be assigned to interaction between structurally equivalent nuclei. Special searches were made in a number of compounds such as  $\text{F}_2\text{PO}(\text{OH})$ , where interaction between the equivalent fluorines might lead to further splitting of the fluorine doublet produced by the phosphorus. However, negative results were always obtained, even under conditions where resolution approached a milligauss. Moreover, the resonance lines observed in all other compounds containing only equivalent magnetic nuclei have been single. This includes not only the compounds mentioned in the preceding sections, but also a very large number of others.<sup>6,8,19</sup> On the other hand, structurally nonequivalent nuclei of the same species, whose resonances are separated by a chemical shift within a molecule, *can* interact to give birth to multiplets. However, the splitting is less than a tenth of that produced by different nuclear species. For example, the proton and fluorine splittings assigned to the phosphorus in  $\text{PH}_3$  and  $\text{PF}_3$  are 0.043 and 0.350 gauss, respectively, while the proton-proton splitting in ethanol is about 0.001 gauss<sup>21</sup> and the fluorine-fluorine splitting in  $\text{BrF}_3$

and  $\text{IF}_5$  is 0.020 gauss. Except for size, the two classes of splitting appear identical.<sup>28</sup>

Cases in which nonequivalent magnetic nuclei in a molecule do *not* interact to give observed multiplets are of several types. In compounds such as  $\text{CH}_3\text{OPF}_2$  and  $\text{F}_2\text{PO}(\text{OH})$ , the fluorine and phosphorus multiplets may be explained without reference to the protons even though the proton magnetic moment is large. But the protons are separated from the fluorine and phosphorus nuclei by one or two other nuclei which must attenuate any interactions to something less than the experimental resolution.<sup>29</sup> In ethanol,<sup>21</sup>  $\text{CH}_3\text{CH}_2\text{OH}$ , the proton lines corresponding to  $\text{CH}_3$  and  $\text{CH}_2$  are multiple, while that from the OH is single with a temperature and concentration dependent chemical shift. Liddel and Ramsey<sup>30</sup> have suggested that since the hydroxyl protons are hydrogen bonded in association complexes, the chemical shift must be averaged over the temperature and concentration dependent dynamic equilibrium state. A similar averaging of the nuclear interactions between the  $\text{CH}_2$  and OH groups would wash out the multiplet structure in the latter; this mechanism could account for the nonmultiplet proton resonances in liquid<sup>19</sup> HF and in the  $\text{HPF}_6$  and  $\text{HBF}_4$  described above.

Magnetic nuclei with electric quadrupole moments usually do not produce multiplets. Thus, in  $\text{PCl}_3$ ,  $\text{PBr}_3$ , and  $\text{PI}_3$ , the phosphorus resonances are single even though the chlorine, bromine, and iodine nuclei have appreciable magnetic moments. However, in these compounds the strong coupling of the electric quadrupole moments of the halogen nuclei with the electrostatic field gradients fixed in the molecule provides a mech-

TABLE V. Multiplet splittings at different applied magnetic fields.

Fluorine compounds	$\text{F}^{19}$ resonance		$\text{P}^{31}$ resonance	
	at 4180 gauss	at 6365 gauss	at 4180 gauss	at 6365 gauss
$\text{CH}_3\text{OPF}_2$	0.328 gauss	0.320 gauss	0.751 gauss	0.740 gauss
$\text{F}_2\text{PO}(\text{OH})$	0.242	0.244	...	0.570
$\text{FPO}(\text{OH})_2$	0.241	0.238	...	...
$\text{HPF}_6$	0.179	0.178	...	0.41
Hydrogen compounds	$\text{H}^1$ resonance		$\text{P}^{31}$ resonance	
	at 4180 gauss	at 6365 gauss	at 4180 gauss	at 6365 gauss
$\text{HPO}(\text{OH})_2$	0.166	0.166	0.407	0.410
$\text{H}_2\text{PO}(\text{OH})$	0.136	0.137	...	0.344

<sup>28</sup> Experiments in progress, with equipment giving milligauss resolution or better, indicate multiplet splitting of chemically shifted components of the proton resonances is the rule rather than the exception in most organic compounds.

<sup>29</sup> This fact can be used as the basis for molecular structure determination. Phosphorous acid,  $\text{H}_2\text{PO}_3$ , is known to be dibasic so it is generally supposed that one of the three protons is bonded directly to phosphorus. [See, e.g., D. M. Yost and H. Russell, Jr., *Systematic Inorganic Chemistry* (Prentice-Hall, Inc., New York, 1944), Chapter 6.] The phosphorus doublet observed in  $\text{H}_2\text{PO}_3$  indicates that indeed one and only one proton is bonded directly to the phosphorus. Similarly, the phosphorus triplet in  $\text{H}_3\text{PO}_3$  confirms that two protons in it are bonded to phosphorus; and in  $\text{FPO}(\text{OH})_2$  and  $\text{F}_2\text{PO}(\text{OH})$  the fluorines are also attached directly to the phosphorus.

<sup>30</sup> U. Liddel and N. F. Ramsey, *J. Chem. Phys.* **19**, 1608 (1951).

anism whereby the magnetic interactions may be averaged over all *relative* orientations of the nuclear moments, giving single phosphorus resonances.<sup>31</sup> The antimony, boron, and vanadium resonances in  $\text{SbF}_6^-$ ,  $\text{BF}_4^-$ , and  $\text{VF}_6^-$  are special cases of this type, since the nuclei have quadrupole moments, while the ionic symmetry prevents electric field gradients at the nuclei. In spite of the apparently similar nature of these ions, the  $\text{B}^{11}$  and  $\text{V}^{51}$  resonances were only slightly broadened, while the antimony was multiplet. The association-dissociation mechanism might be responsible for the difference, as could spin-relaxation effects. In the concluding theoretical section, a discussion is given of some the conditions under which the multiplet-type interactions may average to zero.

The values of the splittings in different compounds are related to the chemical shifts. This may be seen in Fig. 3 where the fluorine splittings are plotted against the chemical shifts, and more clearly in Fig. 4 where the phosphorus splittings and chemical shifts are shown. In general, the correlations between splittings and chemical shifts are too extensive to be accidental. However, different classes of compounds differ in the relation between splittings and chemical shifts. Thus, in Fig. 3, the data for the fluorine resonances in the homologous series  $\text{POCl}_2\text{F}$ ,  $\text{POClF}_2$ , and  $\text{POF}_3$  fall upon a good straight line of negative slope while the related series  $\text{FPO}(\text{OH})_2$ ,  $\text{F}_2\text{PO}(\text{OH})$ , and  $\text{POF}_3$  has a positive slope. Similarly, the phosphorus resonance data for the hydrogen compounds,  $\text{PH}_3$ ,  $\text{H}_3\text{PO}_3$ , and  $\text{H}_3\text{PO}_2$ , in Fig. 4 fall upon a line separate from that for the fluorine compounds.<sup>32</sup> It seems likely, therefore, that the connection between chemical shifts and splittings is an indirect one, both effects being related to the molecular electronic distribution but in somewhat different ways. This question is considered also, in more detail, in one of the following theoretical sections.

TABLE VI. The splittings of different multiplets in the same compound.

Compound	$\text{F}^{19}$ or $\text{H}^1$ splitting*	$\frac{\mu(\text{P}^{31})}{\mu(\text{F}^{19} \text{ or } \text{H}^1)}$
	$\text{P}^{31}$ splitting	
$\text{PF}_3$	0.428	0.430
$\text{CH}_3\text{OPF}_2$	0.434	
$\text{POCl}_2\text{F}$	0.430	
$\text{POClF}_2$	0.425	
$\text{F}_2\text{PO}(\text{OH})$	0.429	
$\text{HPF}_6$	0.434	0.405
$\text{HPO}(\text{OH})_2$	0.402	
$\text{H}_2\text{PO}(\text{OH})$	0.405	
$\text{PH}_3$	0.413	

\* From data obtained at an applied field of 6365 gauss.

<sup>31</sup> Jeffries, Loeliger, and Staub, *Phys. Rev.* **85**, 478 (1952), have reported a very broad titanium triplet resonance line in liquid  $\text{TiCl}_4$ . In this case, it seems likely that the quadrupolar effects would prevent a multiplet of the sort described in the present article.

<sup>32</sup> A discussion of the dependence of the phosphorus chemical shifts upon molecular structure is planned for publication at some future date.

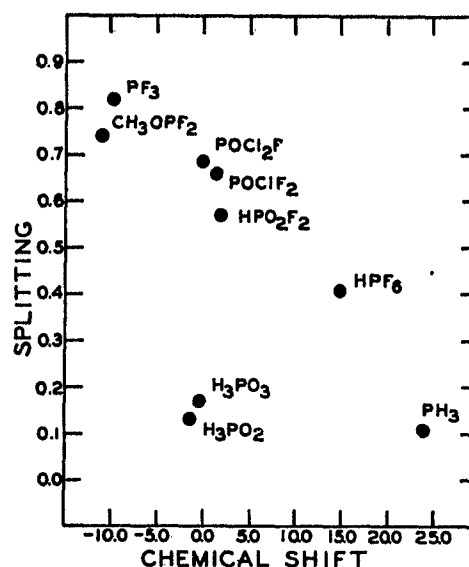


FIG. 4. The multiplet splittings, in gauss, of the phosphorus resonance plotted against the chemical shifts, in units of  $10^4 \times (H_c - H_r)/H_r$ , where  $H_c$  and  $H_r$  are the applied fields required for resonance in the compound and in the aqueous phosphoric acid reference, respectively. The data were obtained at 6365 gauss.

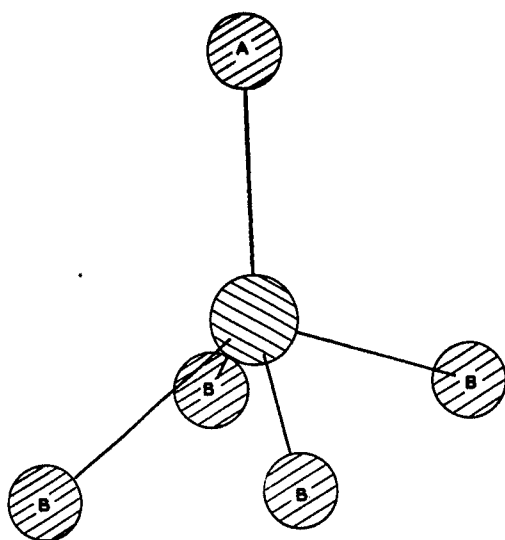
#### THEORETICAL

The experimental results described above show that the multiplets occur despite rapid molecular reorientation and are not produced by interactions between equivalent nuclei, eliminating a direct magnetic dipole-dipole interaction as their cause. Also, the multiplets are independent of applied magnetic field, eliminating a direct second-order interaction.<sup>12</sup> And, finally, their dependence upon the nuclear magnetic moments and the electronic structure of the molecule suggests a second-order process in which one nucleus induces a magnetic moment in the electron distribution in the molecule, the induced moment interacting with the second nucleus.

#### The Dot Product $\mu_1 \cdot \mu_2$

Without inquiring too deeply into the coupling mechanism, one can show that an interaction of the form  $A_{12}\mu_1 \cdot \mu_2$  leads to the essential qualitative aspects of the observed multiplets.  $A_{12}$  is a coupling constant independent of temperature and applied magnetic field, but related to the electronic structure of the system. This form for the interaction can be deduced in the following way. If the nuclei interact by some sort of induced magnetization, the field induced at one nucleus should be proportional to the magnetic moment of the other, and the interaction energy is then proportional to the product of the nuclear moments. Also, since the multiplets persist during rapid molecular reorientations, the interaction must depend on the *relative* orientation of the nuclear moments. The interaction is therefore of the form  $A_{12}\mu_1 \cdot \mu_2$ . Moreover, since the



FIG. 5. Molecular model of  $\text{BrF}_5$ .

interactions of the electrons with the applied magnetic field and with thermal jostlings are small compared to the electronic energies associated with the multiplet interaction, the coupling constant  $A_{12}$  should be unaffected by applied field and temperature.

The Hamiltonian for the dot product coupling may be determined by considering a typical molecule, such as  $\text{BrF}_5$ . As shown in Fig. 5, the five fluorines are divided into two groups; group  $A$  is the single fluorine at the apex of a tetragonal pyramid, while group  $B$  contains the four equivalent nuclei at the corners of the square base. The bromine nucleus can be ignored because of the effects of quadrupole coupling. Now, interactions can occur between groups  $A$  and  $B$ , and also among the nuclei in  $B$ . The structural equivalence of the  $B$  requires that each  $B$  has the same interaction with  $A$ , even though different pairs of  $B$  may differ in their interactions, e.g., adjacent pairs contrasted with opposite pairs. In many cases, such as  $\text{PF}_5$ , groups  $A$  and  $B$  represent different nuclear species, not merely chemically nonequivalent nuclei of the same species as in  $\text{BrF}_5$ . The results are generalized readily to more than two groups of nuclei.

The required Hamiltonian is

$$\mathcal{H} = \gamma_A \hbar F_{Ax} H_A + \gamma_B \hbar F_{Bx} H_B + a \mathbf{F}_A \cdot \mathbf{F}_B + \sum_{i,j=A \text{ and } i,j=B} b_{ij} \mathbf{I}_i \cdot \mathbf{I}_j, \quad (1)$$

where  $\mathbf{F}_A = \sum_{i=A} \mathbf{I}_i$  is the total spin angular momentum of group  $A$ ,  $\mathbf{F}_B = \sum_{i=B} \mathbf{I}_i$ , and  $F_{Ax}$  and  $F_{Bx}$  are the components along the static fields  $H_A$  and  $H_B$  at nuclei  $A$  and  $B$ .  $H_A$  and  $H_B$  are different, of course, because of chemical shifts in the nuclear magnetic shielding. The solution of Eq. (1) is complicated by the last term, which involves the interactions within each given group.

However, this term does not represent observable effects and hence may be omitted from the Hamiltonian, as we will now show by a direct calculation of the observable measured in our experiments.

#### Interactions between Equivalent Nuclei

The sample is placed in an rf coil whose axis, the  $x$  axis, is transverse to the static field. The component of total nuclear magnetization along the coil axis is measured, that is the equipment responds to the expectation value  $(\Psi, M_x \Psi)$  of the operator  $M_x$ , where

$$M_x = \gamma_A \hbar F_{Ax} + \gamma_B \hbar F_{Bx}. \quad (2)$$

$(\Psi, M_x \Psi)$  varies with time, inducing voltages in the coil at the nuclear resonance frequencies. The time dependent Schrodinger equation for the system may be written as

$$-\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} = (\mathcal{H}_0 + \mathcal{H}_1) \Psi, \quad (3)$$

where

$$\mathcal{H}_0 = \gamma_A \hbar F_{Ax} H_A + \gamma_B \hbar F_{Bx} H_B + a \mathbf{F}_A \cdot \mathbf{F}_B + \gamma_A \hbar F_{Ax} H_{Ax} \sin \omega t + \gamma_B \hbar F_{Bx} H_{Bx} \sin \omega t \quad (4)$$

and

$$\mathcal{H}_1 = \sum_{i,j=A \text{ and } i,j=B} b_{ij} \mathbf{I}_i \cdot \mathbf{I}_j. \quad (5)$$

The terms in  $H_{Ax}$  and  $H_{Bx}$  are from the alternating magnetic field produced in the coil by the external oscillator of angular frequency  $\omega$ . We need to show that  $(\Psi, M_x \Psi)$  is not influenced by  $\mathcal{H}_1$ , the interactions among the equivalent nuclei.

$\mathcal{H}_1$  does not depend explicitly on time. A canonical transformation is performed to a new wave function:

$$\Phi = \exp(i\mathcal{H}_1 t / \hbar) \Psi \quad (6)$$

obeying the equation

$$\mathcal{H}_0' \Phi = -\frac{\hbar}{i} \frac{\partial \Phi}{\partial t}, \quad (7)$$

where

$$\mathcal{H}_0' = \exp(i\mathcal{H}_1 t / \hbar) \mathcal{H}_0 \exp(-i\mathcal{H}_1 t / \hbar), \quad (8)$$

and since  $\mathcal{H}_0$  and  $\mathcal{H}_1$  commute,

$$\mathcal{H}_0' \Phi = -\frac{\hbar}{i} \frac{\partial \Phi}{\partial t}. \quad (9)$$

Therefore,  $\Phi$  unfolds in time as if  $\mathcal{H}_1$  were not present, and represents the solution of the simplified problem in which there is zero interaction among nuclear spins in the same group. The observed quantity  $(\Psi, M_x \Psi)$  can be expressed in terms of  $\Phi$ ,

$$\begin{aligned} (\Psi, M_x \Psi) &= [\exp(-i\mathcal{H}_1 t / \hbar) \Phi, M_x \exp(-i\mathcal{H}_1 t / \hbar) \Phi] \\ &= [\Phi, \exp(i\mathcal{H}_1 t / \hbar) M_x \exp(-i\mathcal{H}_1 t / \hbar) \Phi], \quad (10) \end{aligned}$$

and since  $\mathcal{H}_1$  and  $M_z$  commute,

$$(\Psi, M_z \Psi) = (\Phi, M_z \Phi). \quad (11)$$

This is the desired result, as it says the behavior of  $M_z$  as a function of time is the same as it would be if there were no interactions among spins in the same group. Note that this proof makes no statement about stationary states, for the problem is a dynamical one.<sup>23</sup> Moreover, the proof is exact and does not require the interaction constants  $b_{ij}$  in Eq. (5) to be small. The physical significance of this result is that while the apparatus detects the combined effects of all the nuclear moments, the coupling among the spins of a given group causes them to precess about one another in some complicated way, but leaves the resultant total nuclear magnetization unchanged. It is essential that any theoretical model for the coupling have this property, otherwise the coupling among equivalent nuclei would predict multiplets where none have been found experimentally.

#### Solution of the Simplified Hamiltonian

The Hamiltonian, simplified by omission of the coupling between equivalent nuclei, is

$$\mathcal{H} = \gamma_A \hbar F_{A_z} H_A + \gamma_B \hbar F_{B_z} H_B + a \mathbf{F}_A \cdot \mathbf{F}_B. \quad (12)$$

In solving this equation, the last term  $a \mathbf{F}_A \cdot \mathbf{F}_B$  may be approximated by  $a F_{A_z} F_{B_z}$ .<sup>24</sup> This is a first-order perturbation calculation, which is valid providing

$$|\gamma_A \hbar H_A - \gamma_B \hbar H_B| \gg a, \quad (13)$$

a condition satisfied in our experiments. With this approximation, the simplified Hamiltonian, Eq. (12), becomes

$$\mathcal{H} = \gamma_A \hbar F_{A_z} H_A + \gamma_B \hbar F_{B_z} H_B + a F_{A_z} F_{B_z}. \quad (14)$$

Clearly, the operators  $F_{A_z}^2$ ,  $F_{B_z}^2$ ,  $F_{A_z}$ , and  $F_{B_z}$  commute with the Hamiltonian and with one another, so they may be used to describe the system. If there are  $n_A$  nuclei of spin  $I_A$  in group  $A$  and  $n_B$  nuclei of spin  $I_B$  in

group  $B$ , the appropriate quantum numbers are  $F_A$ ,  $M_A$ ,  $F_B$ , and  $M_B$ , where  $F_A = n_A I_A$ ,  $n_A I_A - 1, \dots, 0$  or  $\frac{1}{2}$ , and  $M_A = F_A, F_A - 1, \dots, -F_A$ , with similar expressions for  $F_B$  and  $M_B$ . The energy levels are then

$$E = \gamma_A \hbar M_A H_A + \gamma_B \hbar M_B H_B + a M_A M_B. \quad (15)$$

In the approximation of the perturbation treatment used, the selection rules for transitions are  $\Delta F_A = \Delta F_B = 0$ ;  $\Delta M_A = \pm 1$ ,  $\Delta M_B = 0$ , or  $\Delta M_A = 0$ ,  $\Delta M_B = \pm 1$ . Resonance absorption lines for nuclei  $A$  and  $B$  occur at angular frequencies

$$\omega_A = \gamma_A H_A + \frac{a}{\hbar} M_B \quad (16)$$

and

$$\omega_B = \gamma_B H_B + \frac{a}{\hbar} M_A.$$

For instance,  $\omega_A$  consists of a family of components, with spacing  $a/\hbar$ , centered at  $\gamma_A H_A$ . The number of components and their relative intensities are given by the number and relative probabilities of the various values of  $M_B$ , in agreement with the experimental facts.

Our original conclusions about the form of the inter-nuclear coupling enables us to write the constant  $a$  as

$$a = c \gamma_A \gamma_B, \quad (17)$$

where  $c$  is a constant. By combining this with Eq. (16), it is seen that transitions occur at

$$\omega_A = \gamma_A \left( H_A + \frac{c}{\hbar} \gamma_B M_B \right) \quad (18)$$

and

$$\omega_B = \gamma_B \left( H_B + \frac{c}{\hbar} \gamma_A M_A \right).$$

The multiplet splitting of  $A$ , expressed in terms of an equivalent static field,  $\delta H_A$  is  $c \gamma_B / \hbar$ , while  $\delta H_B$  is  $c \gamma_A / \hbar$ . And as a final result

$$\delta H_A / \delta H_B = \gamma_B / \gamma_A. \quad (19)$$

If both nuclei have the same spin, this ratio is the same as the ratio of the magnetic moments, in further agreement with the experiments on  $\text{H}^1$ ,  $\text{F}^{19}$ , and  $\text{P}^{31}$ . The only case reported in which splittings have been observed for nuclei with different spins is  $\text{SbF}_6^-$ , where the data are in qualitative agreement<sup>17</sup> with Eq. (19).

#### The Coupling Mechanism

The dot product coupling discussed above has the desired qualitative characteristics and accounts for effects unexplained by other hypotheses. The next major question concerns the magnetization induced in the molecule by the magnetic nuclei. This magnetization is the basic mechanism for the coupling, and could involve either the electron orbital or the electron spin magnetic moments, or both. Second-order perturbation

<sup>23</sup> This result is directly applicable, therefore, to the spin echo experiment, where the Hamiltonian is the same except that  $H_{A_z}$  and  $H_{B_z}$  are zero most of the time. The switching on and off of the rf field does not affect the time dependence of  $\mathcal{H}_1$  or the commutability of  $\mathcal{H}_1$  with  $\mathcal{H}_0$  and  $M_z$ .

<sup>24</sup> It is not justifiable to make a similar approximation to the complete Hamiltonian, Eq. (1), by replacing the last term, Eq. (5), with the product of the  $z$  components; this gives the erroneous result that coupling among equivalent nuclei would produce multiplets. A simple physical argument will serve to show the difference between the two situations. It is possible, if two spins are in group  $A$ , for example, to find a rotating reference frame in which the effect of the external field is transformed to zero at both spins. In this frame, the dot product coupling would cause the two spins to precess about one another, their vector resultant remaining constant. On the other hand, if the spins are in different groups, a rotating reference frame transforming the external field at  $A$  to zero will not transform  $H_B$  to zero. The motion of  $B$  will then be predominantly precession about that fraction of  $H_B$  remaining. The additional field due to coupling with species  $A$  will add vectorially to this residual of  $H_B$ , with only the component of  $A$ 's field along  $H_B$  important to first order.

theory is required to estimate the relative magnitudes of such magnetization, since to first order there is zero electron orbital and spin magnetization in any direction.

### Orbital Effects

$M_A^{(0)}$ , the orbital moment induced by a nuclear moment  $A$ , is of order of magnitude

$$M_A^{(0)} \sim \frac{\mu_A \beta^2}{\Delta E} \langle 1/r_A^3 \rangle_n, \quad (20)$$

where  $\beta$  is the Bohr magneton;  $\Delta E$ , the energy to an excited electronic orbital; and  $\langle 1/r_A^3 \rangle_n$  is the average inverse cube of the distance from a valence electron to nucleus  $A$ . If  $R$  is the internuclear distance between  $A$  and  $B$ , the induced electron orbital moment will interact with the nuclear moment of  $B$  with an energy of order

$$\frac{M_A^{(0)} \mu_B}{R^3} = \frac{\mu_A \mu_B \beta^2}{R^3 \Delta E} \langle 1/r_A^3 \rangle_n. \quad (21)$$

This calculation assumes the induced orbital moment does not average to zero over the molecular tumbling, hence requires anisotropic polarizability.

### Electron Spin Effects

Naively, one might suppose the electron spin moments could be neglected, as is allowed in Ramsey's treatment<sup>9</sup> of chemical shifts in nuclear magnetic shielding in molecules, or that at most the spin effects would be the same order of magnitude as the orbital, except for orbital  $S$  states. However, Ramsey and Purcell<sup>10</sup> have pointed out that a more careful analysis is required. In a covalent bond, the electron spins of the two shared electrons are paired. The spin magnetization induced by the interaction of nucleus  $A$  with its electron is

$$M_A^{(0)} \sim \frac{\mu_A \beta^2}{\Delta E} \langle 1/r_A^3 \rangle_n, \quad (22)$$

where  $\Delta E$  is now the energy to an excited electronic spin state. But when the electron spin is up for the electron on one atom, it is down for the other electron on the second atom, so there must be an identical spin magnetization,  $M_B^{(0)}$  in the opposite direction transmitted to  $B$ 's electron. The interaction energy of this moment with nucleus  $B$  is

$$M_B^{(0)} \mu_B \langle 1/r_B^3 \rangle_n = \frac{\mu_A \mu_B \beta^2}{\Delta E} \langle 1/r_A^3 \rangle_n \langle 1/r_B^3 \rangle_n. \quad (23)$$

This energy is larger than the orbital interaction, Eq. (21), in the ratio  $R^3 \langle 1/r_B^3 \rangle_n$ , a factor of ten to twenty in many cases, assuming the spin and orbital  $\Delta E$ 's to be

<sup>10</sup> N. F. Ramsey and E. M. Purcell, Phys. Rev. 85, 143 (1952).

comparable. Detailed calculations given below show that the electron spin terms give an order of magnitude comparable to the experimental results.

### Calculation of the Electron Spin Coupling

The complete Hamiltonian for the electron-nuclear spin interactions in a molecule has been given previously.<sup>10,11</sup> The required second-order interaction energy of the nuclear magnetic moments with the electron spin moments is given by

$$\Delta E_{AB} = A v_\lambda \sum \frac{(0|\mathfrak{F}_A|n)(n|\mathfrak{F}_B'|0) + (0|\mathfrak{F}_B'|n)(n|\mathfrak{F}_A|0)}{E_n - E_0}, \quad (24)$$

where  $\mathfrak{F}_A$  is the interaction between nucleus  $A$  and the electrons, and  $\mathfrak{F}_B$  is that between nucleus  $B$  and the electrons. The Hamiltonian contains two types of terms representing nucleus-electron interaction,  $\mathfrak{F}_2$  and  $\mathfrak{F}_3$  in the notation of Ramsey and Purcell,<sup>10</sup> one representing  $S$  orbital electronic states, the other non- $S$  states. The prime on  $\mathfrak{F}_B$  in Eq. (24) indicates that cross terms between  $\mathfrak{F}_2$  and  $\mathfrak{F}_3$  may have to be computed. " $A v_\lambda$ " signifies an average over all spatial molecular orientations " $\lambda$ ."  $E_0$  is the energy of the ground electronic state whereas  $E_n$  is that of the  $n$ th excited electronic state. An approximation to  $\Delta E_{AB}$  is obtained by replacing  $E_n - E_0$  by an average energy difference  $\Delta E$ , and making use of the diagonal sum property to eliminate the excited states. This gives

$$\Delta E_{AB} = A v_\lambda \frac{(0|\mathfrak{F}_A \mathfrak{F}_B'|0) + (0|\mathfrak{F}_B' \mathfrak{F}_A|0)}{\Delta E}. \quad (25)$$

The magnitude of  $\Delta E$  depends upon the type of excited state to which  $\mathfrak{F}_A$  and  $\mathfrak{F}_B$  couple. The excited states may involve a change in the orbital part of the wave function, the spin part, or both. When coupling occurs, the excited state mixed in corresponds to a more favorable electron spin alignment, that is, the perturbed wave function has a net spin polarization. Such states are formed by mixing the electron spin triplet states in with the singlet ground state. Addition of other singlet states will not produce a net polarization of the electron spins. So the appropriate energy  $\Delta E$  is that needed to unpair the electron spins.

Before attempting numerical calculations with Eq. (25), two useful theorems will be proved. (1) To a good approximation the electron-nuclear spin interaction can be calculated for each atom separately. (2) Only the two electrons involved directly in the covalent bond need be considered.

<sup>11</sup> A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) A205, 136 (1951).

*Proof of Theorems*

The ground-state molecular electronic wave function is needed to evaluate integrals of the type in Eq. (25). A Heitler-London product of atomic orbitals should be a good approximation for our purpose, since the radial dependence of the coupling is  $(1/r^3)$ , which is most important close to the nucleus where the atomic orbitals are most accurate. The angular dependence is important principally in averaging over molecular orientations; this may be accomplished by hybridizing the atomic orbitals to give the required molecular symmetry.

Accordingly,  $\psi$ , the ground-state wave function for a molecule with  $N$  electrons, is taken to be a linear combination of functions

$$\phi_k = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P a(\alpha)_1 b(\beta)_2 c(\alpha)_3 d(\beta)_4 \dots, \quad (26)$$

where  $a, b, c, \dots$  represent the spatial dependence of the individual hybridized orbitals; subscripts, 1, 2,  $\dots, \nu$  label the  $N$  electrons;  $P$  is the permutation operator; and  $\alpha$  and  $\beta$  are the spin up and spin down functions. The other  $\phi$ 's included in  $\psi$  differ only in interchanges of spin functions. In practice, the closed shell orbitals are omitted, and the  $N$  electrons are simply the valence electrons.  $\psi$  may be written as the product of  $\psi_0$ , the orbital part, and  $\psi_s$ , the spin part, with the permutation operator applied to satisfy the Pauli principle, so that

$$\psi = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P \psi_0 \psi_s. \quad (27)$$

With this function, we must calculate integrals such as

$$\int \psi^* \sum_{i,j} \mathfrak{G}_{Ai} \mathfrak{G}_{Bj'} \psi d\tau, \quad (28)$$

where the integration is over all electron spatial and spin coordinates, and  $\mathfrak{G}_{Ai}$  is the interaction between nucleus  $A$  and electron  $i$ , etc. Introducing  $\psi$  from Eq. (27), the integral equals

$$\begin{aligned} & \frac{1}{N!} \int \sum_P (-1)^P P \psi_0^* \psi_s^* \\ & \quad \times \sum_{i,j} \mathfrak{G}_{Ai} \mathfrak{G}_{Bj'} \sum_P (-1)^P P \psi_0 \psi_s d\tau \\ & = \int \psi_0^* \psi_s^* \sum_{i,j} \mathfrak{G}_{Ai} \mathfrak{G}_{Bj'} \sum_P (-1)^P P \psi_0 \psi_s d\tau. \end{aligned} \quad (29)$$

The function  $\psi_0$  is  $a(1)b(2)\dots n(\nu)$ , where  $a(1)$  means electron 1 is in orbital  $a$ , etc. For  $\psi_s$ , the permutation  $P$  gives contributions to Eq. (29) that are small unless electron  $i$  is in an orbital on atom  $A$  and electron  $j$  is in an orbital on  $B$ . Other terms are small because  $\mathfrak{G}_{Ai}$  and  $\mathfrak{G}_{Bj}$  depend strongly on the distance from the nucleus; the only permutations that are not small for this reason

involve exchange of electrons on a given atom. But these terms are likewise negligible if  $\int a(1)^* b(1) d\tau$ , and similar integrals are small; in many cases they are zero since  $a$  and  $b$  are orthogonal functions, and, in general, they can be ignored. With these reductions, Eq. (29) becomes simply

$$\int \psi_0^* \psi_s^* \sum_{i,j} \mathfrak{G}_{Ai} \mathfrak{G}_{Bj'} \psi_0 \psi_s d\tau. \quad (30)$$

The next step is to integrate over either the spin or spatial coordinates. The spatial integrations are over each atom separately; this proves theorem (1). After such integration the problem is reduced to the electron spin manifold.

For further progress,  $\psi_s$  is required, and is assumed to have the form

$$\begin{aligned} \psi_s = & \frac{1}{\sqrt{2}} \{ \alpha(1)\beta(2) - \beta(1)\alpha(2) \} \\ & \times \frac{1}{\sqrt{2}} \{ \alpha(3)\beta(4) - \beta(3)\alpha(4) \} \dots \end{aligned} \quad (31)$$

where electrons 1 and 2 share a bond, 3 and 4 another, etc. In effect, this implies that the covalent bonds completely dominate the spin coupling. The various terms  $\mathfrak{G}_{Ai} \mathfrak{G}_{Bj'}$  involve products such as  $S_{zi} S_{zj'}$  between the different electron spin operators. This is a sort of correlation between the spins, which we expect for electrons in the same bond since when one spin is up the other is down. However, the  $\psi_s$  chosen does not correspond to any correlation between electron spins not in the same bond, as can be shown by explicit calculation. Therefore, if Eq. (31) is used as the spin function, we need consider only terms arising from the orbitals bonding atom  $A$  to atom  $B$ . This is theorem (2). This approximation greatly simplifies the calculations.

*Numerical Results*

In the case of  $\text{PF}_3$ , we assume  $p$  bonds for both the fluorine and phosphorus. Taking the  $z$  axis along one bond, the phosphorus-fluorine interaction is proportional to

$$I_{Pz} I_{Fz} + I_{Py} I_{Fy} + 4I_{Px} I_{Fx}, \quad (32)$$

where  $I_{Px}$  is the  $x$  component of the phosphorus spin.<sup>37</sup> The bond is assumed to have cylindrical symmetry so the  $x$  and  $y$  components are symmetrical. The axes we have chosen tumble with the molecule. We must therefore express the spin components in terms of axes fixed in space, and perform an average over molecular orientations, since the tumbling frequency in the liquid is extremely high. When this is done for  $\text{PF}_3$ , the inter-

<sup>37</sup> The calculation giving Eq. (32) is very similar to that involved in the anisotropic nucleus-electron interaction treated by Abragam and Pryce, reference 36.

action energy is found to be

$$(1/\Delta E) \left( \frac{16}{25} \beta^2 \langle 1/r_F^3 \rangle_M \langle 1/r_P^3 \rangle_M \gamma_F \gamma_P \hbar^2 \mathbf{I}_F \cdot \mathbf{I}_P \right). \quad (33)$$

Values for  $\langle 1/r_P^3 \rangle_M$  and  $\langle 1/r_F^3 \rangle_M$  may be obtained from Sternheimer's paper,<sup>38</sup> and when substituted in Eq. (33), give a splitting  $\Delta H_P = 3.0/\Delta E$  gauss, where  $\Delta E$ , the energy to unpair the bonding electron spins, is in electron volts. Reasonable values for  $\Delta E$  are of the order of an electron volt or so, which gives satisfactory agreement with the experimental  $\Delta H_P$  of 0.82 gauss.

For  $\text{PH}_3$ , assuming pure  $s$  and  $p$  orbitals for the hydrogen and phosphorus, respectively, the molecular tumbling makes the interaction vanish. However, the bond angles in  $\text{PH}_3$  are greater than  $90^\circ$ , indicating some  $s$  character in the phosphorus orbitals, which can account for the small splittings observed. For  $\text{H}_2\text{PO}(\text{OH})$  and  $\text{HPO}(\text{OH})_2$ , the phosphorus orbitals used in the P-H bonds should contain a fair amount of  $s$  character since the orbitals available are  $sp^3d$ . The larger proton splittings in these compounds, compared to  $\text{PH}_3$ , are therefore to be expected; the phosphorus  $d$  orbital does not add to the splitting since its interaction with the hydrogen  $s$  orbital averages to zero over the molecular tumbling.

The general trends among the fluorine compounds are explained in a similar manner. The P-F splitting in a compound is determined primarily by the amount of  $p$  character in the phosphorus orbital, since the  $s$  does not couple to the fluorine  $p$  electron when averaged over molecular tumbling. The  $d$  terms are neglected because of the smallness of the  $d$  functions near the origin. Actually, cross terms between  $s$  and  $d$  orbitals on the phosphorus can couple, but their effect is rather small compared to that of a  $p$  orbital. The estimated ratios of the phosphorus splittings,  $\text{PF}_3$  to  $\text{POCl}_2\text{F}$  to  $\text{PF}_5$  is 0.82 to 0.62 to 0.49; the experimental values are 0.82 to 0.68 to 0.41. In these estimates, the same value of  $\Delta E$  was assumed and also that there was about as much  $p$ -character in the  $\text{POCl}_2\text{F}$  bond as in an  $sp^3$  hybrid. In the case of  $\text{PF}_5$ , the bond orbitals are not known. Duffy<sup>39</sup> lists a possible set, those for a trigonal bipyramid. These predict a splitting of the  $\text{F}^{19}$  resonance of about 0.17 gauss relative to 0.35 gauss in  $\text{PF}_3$ . The experimental value is 0.23. It is interesting to note that both the chemical shift and multiplet data imply that all bonds in  $\text{PF}_5$  are equivalent.

Cases such as  $\text{BrF}_3$  and  $\text{IF}_5$  are more difficult to analyze since the interacting nuclei are not bonded directly to one another. The coupling might occur via the weak spin-spin interactions of the electrons in the separate X-F bonds; however, this mechanism cannot

be estimated directly by the procedure developed above since it requires the terms discarded by assuming Eq. (31) for  $\psi$ . Another way to describe the situation is in terms of an electron spin moment induced by one fluorine nucleus on the intervening X atom, which then couples with a second fluorine. This mechanism gives significant coupling only if the moment induced on X varies with the orientation of the fluorine moment relative to the X-F bond direction, otherwise the coupling averages to zero over the molecular tumbling. Such anisotropy is present in  $\text{BrF}_3$  and  $\text{IF}_5$ , and the corresponding F-F splitting has been estimated to be a few per cent of the P-F in  $\text{PF}_3$ . This result compares favorably with the respective experimental values of 0.02 and 0.82 gauss.

The preceding numerical calculations are approximate at best. Besides the approximations inherent in the method, in evaluating the  $\langle 1/r^3 \rangle_M$  terms, and in  $\Delta E$ , most bonds have an appreciable amount of ionic character, which may vary in different compounds. For instance, the P-F bond is probably only about 40 percent covalent; and the 60 percent ionic character would not participate in the splitting. However, the approximate results do provide simple explanations for the observed general trends, and the values are certainly of the right order of magnitude. More refined calculations of this sort are of potential interest and value for investigating the dependence of bond hybridization upon molecular structure.

### Spin Relaxation Effects

In the experimental work, multiplets were not found in a number of cases where the interactions described above could occur. This is reasonable, for even though nuclei  $A$  and  $B$  are coupled together, rapid random transitions of the spin of  $A$  among its various spatial orientations can smear out the multiplet structure of  $B$ 's resonance. In fact, if  $A$ 's transitions become rapid enough, the resonances of both  $A$  and  $B$  will be unaffected by the coupling and  $B$  will be a single narrow line. Processes inducing transitions include spin-lattice and spin-spin relaxation; also, a similar effect would be produced by an actual chemical exchange of atoms between two molecular species. In these processes, and others of a similar nature, there is some time,  $\tau$ , which characterizes the flipping or rate process of say nucleus  $A$ . If the multiplet splitting in frequency units is  $\delta\omega$ , then when  $\tau$  is  $1/\delta\omega$ , the multiplet structure starts to disappear. We will derive this result by considering the particular case of spin-lattice relaxation.

To study the relaxation effects, we shall make use of the Bloch equations,<sup>40</sup> including an extra term to represent the nuclear coupling field. The modified Bloch

<sup>38</sup> R. Sternheimer, Phys. Rev. **84**, 244 (1951).

<sup>39</sup> G. H. Duffy, J. Chem. Phys. **17**, 196 (1949).

<sup>40</sup> F. Bloch, Phys. Rev. **70**, 460 (1946).

equations then become

$$\begin{aligned} \frac{du}{dt} + \left( \Delta\omega + \frac{\delta\omega}{2} \right) v &= -\frac{u}{T_2}, \\ \frac{dv}{dt} - \left( \Delta\omega + \frac{\delta\omega}{2} \right) u &= -\frac{v}{T_2} - \omega_1 M_z, \\ \frac{dM_z}{dt} - \omega_1 v &= -\frac{(M_z - M_0)}{T_1}. \end{aligned} \quad (34)$$

The quantities  $u$ ,  $v$ , and  $M_z$  are the three components of nuclear magnetization along a set of axes rotating with angular frequency  $\gamma H_0$  in the static field  $H_0$ .  $\omega_1 = \gamma H_1$ , where  $H_1$  is the strength of the rotating magnetic field (that is, one of the two rotating components into which the linearly polarized field may be decomposed).  $H_1$  is taken as parallel to  $u$ .  $\Delta\omega$  is  $\gamma H_0 - \omega$ , where  $\omega$  is the angular frequency of the alternating magnetic field.

If, for concreteness, we consider the P-F case,  $u$ ,  $v$ , and  $M_z$  can be the fluorine nuclear magnetization, and  $\delta\omega/2$  then represents the local field due to the phosphorus. There are three more equations similar to Eq. (34) except for replacement of  $\delta\omega$  with  $-\delta\omega$ . These latter equations correspond to the other orientation of the phosphorus spin. (If the spin is greater than  $\frac{1}{2}$ , correspondingly more equations are needed). Our treatment is then a mixture of the classical (the Bloch equations) and the quantum (the discrete local field correction.) This mixture provides a simple way of taking into account the internuclear coupling. The modified Bloch equations are readily solved if one assumes  $\omega_1$  is small (no saturation) since then  $M_z \cong M_0$ . If we call  $u + iv = G$ , an equation for  $G$  is obtained by adding the first equation to  $i$  times the second.  $G$  obeys the equations

$$\begin{aligned} \frac{dG_+}{dt} + \left[ \frac{1}{T_2} - i \left( \Delta\omega + \frac{\delta\omega}{2} \right) \right] G_+ &= -i\omega_1 M_0 \\ \text{and} \quad \frac{dG_-}{dt} + \left[ \frac{1}{T_2} - i \left( \Delta\omega - \frac{\delta\omega}{2} \right) \right] G_- &= -i\omega_1 M_0, \end{aligned} \quad (35)$$

where  $G_+$  and  $G_-$  denote  $G$  for the two phosphorus spin orientations. To follow  $G$  in time we consider these two equations. While  $+\delta\omega$  applies,  $G$  obeys the  $G_+$  equation. When the phosphorus spin flips,  $G$  obeys the  $G_-$  equation. The solutions join on with the boundary condition that  $G$  is continuous, since the fluorine magnetization does not change when the phosphorus spin flips.

The problem is to find the behavior of  $G$  for a given fluorine as its phosphorus spin is alternately up and down, and then to perform the appropriate average over the various phosphorus life histories of different molecules to give the average fluorine magnetization at any time. We begin by considering one particular

fluorine nucleus. We shall start studying the behavior of  $G$  at the time the phosphorus spin flips to the up position; that is, from the time the  $G_+$  equation holds. For convenience, let us define  $\alpha_+$  and  $\alpha_-$  as

$$\begin{aligned} \alpha_+ &\equiv \frac{1}{T_2} - i \left( \Delta\omega + \frac{\delta\omega}{2} \right), \\ \alpha_- &\equiv \frac{1}{T_2} - i \left( \Delta\omega - \frac{\delta\omega}{2} \right). \end{aligned} \quad (36)$$

Then if  $t=0$  is the time of the phosphorus spin transition, we find

$$G_+ = -\frac{i\omega_1 M_0}{\alpha_+} (1 - e^{-\alpha_+ t}) + G_{0+} e^{-\alpha_+ t}, \quad (37)$$

where  $G_{0+}$  is the value of  $G$  at  $t=0$ .

At any time there is a group of fluorine spins which had an initial value  $G_{0+}$ , and which were "formed" a time  $t$  earlier. The probability that a phosphorus spin orientation will have lasted a time between  $t$  and  $t+dt$  is  $(1/\tau)e^{-t/\tau}dt$  where  $\tau$  is the mean life of phosphorus in a given spin state. We can therefore compute  $\bar{G}_+$ , the average value at any given time of those  $G_+$ 's formed with  $G=G_{0+}$  initially.  $\bar{G}_+$  is given by the equation

$$\bar{G}_+ = \int_0^\infty \frac{e^{-t/\tau}}{\tau} G_+(t) dt = -\frac{i\omega_1 M_0 \tau}{1 + \alpha_+ \tau} + \frac{G_{0+}}{1 + \alpha_+ \tau}. \quad (38)$$

Different fluorine nuclei will have different values of  $G_{0+}$ . So far we have considered only those with a given value of  $G_{0+}$ . We must now average over all the possible values of  $G_{0+}$  to get  $\langle \bar{G}_+ \rangle_{av}$ , the average value of  $G_+$  we would find at any time.

What is the average value of  $G_{0+}$ ? This question is easy to answer if we remember that  $G$  does not change when the phosphorus spin flips. Therefore the average value of  $G_{0+}$  is merely the average value of  $G_-$  at the time of a flip. However, a phosphorus spin is as likely to flip at any one time as at any other. The average value of  $G_-$  at the time of a spin flip is therefore the average value of  $G_-$  at any time, namely  $\langle \bar{G}_- \rangle_{av}$ . Thus we get the equation

$$\langle \bar{G}_+ \rangle_{av} = \frac{\langle \bar{G}_- \rangle_{av}}{1 + \alpha_+ \tau} - \frac{i\omega_1 M_0 \tau}{1 + \alpha_+ \tau}, \quad (39)$$

and a corresponding equation, by symmetry,

$$\langle \bar{G}_- \rangle_{av} = \frac{\langle \bar{G}_+ \rangle_{av}}{1 + \alpha_- \tau} - \frac{i\omega_1 M_0 \tau}{1 + \alpha_- \tau}. \quad (40)$$

Since at any time half the phosphorus nuclei will be in each spin orientation, the average value of  $G$ ,  $\langle \bar{G} \rangle_{av}$ , will

be given by

$$\langle \tilde{G} \rangle_{av} = \frac{1}{2} (\langle \tilde{G}_+ \rangle_{av} + \langle \tilde{G}_- \rangle_{av}) \\ = \frac{-\omega_1 M_0 \tau \{2 + [(1/T_2) - i\Delta\omega] \tau\}}{(1 + \alpha_+ \tau)(1 + \alpha_- \tau) - 1} \quad (41)$$

When  $\tau$  is very large we have

$$\langle \tilde{G} \rangle_{av} = \frac{-\omega_1 M_0}{2} \left\{ \frac{1}{(1/T_2) - i[\Delta\omega + (\delta\omega/2)]} \right. \\ \left. + \frac{1}{(1/T_2) - i[\Delta\omega - (\delta\omega/2)]} \right\} \quad (42)$$

a double resonance of total splitting  $\delta\omega$ .

When  $\tau$  is very small we get

$$\langle \tilde{G} \rangle_{av} = \frac{i\omega_1 M_0}{(1/T_2) - i\Delta\omega} \quad (43)$$

which represents a single resonance of twice the intensity of the double ones above. The single line for small  $\tau$  results from the averaging of the phosphorus spin. The transition from long to short  $\tau$  occurs when  $\tau\delta\omega \sim 1$ , as can be shown from Eq. (41). For typical cases, this relation shows that splittings would disappear for  $\tau$  a few tenths of a millisecond.

Examples of the lack of multiplet structure probably explained by relaxation effects are the apparent absence of an interaction between Br and F in  $\text{BrF}_3$ , or between P and Cl in  $\text{POClF}_2$ . In both cases we are dealing with

an atom (Br or Cl) whose nucleus possesses an electric quadrupole moment, situated at a site in a molecule at which there is an electric field gradient. The Br (or Cl) spin-lattice relaxation time is probably very short, since the quadrupolar coupling provides a potent relaxation mechanism. Even when there is no static electric field gradient, a quadrupole moment may still provide the dominant relaxation process. We may well fail to observe splittings even when there is no quadrupole "splitting" present.

We should mention one other point related to electric quadrupole interactions, but not a relaxation process, however. If we have a molecule in which the quadrupole coupling frequency is greater than the molecular tumbling frequency, another effect may arise. The nuclear spin is then dragged around by the molecular tumbling. No splitting would be observed in this case either.

#### ACKNOWLEDGMENT

We wish to express our appreciation to Dr. E. L. Hahn for several interesting and valuable discussions and communications, including advance notification of the significant spin-echo experiments at Stanford. We thank Dr. Wayne E. White of Ozark-Mahoning Company, Mr. R. Mattair of Oldbury Electro-Chemical Company, and Professor D. R. Martin for their generosity in supplying many of the compounds. The equipment was provided mainly by grants-in-aid from Research Corporation. Mr. R. E. McClure assisted in a number of the measurements; Mr. T. R. Carver assisted in the early field dependence measurements.

## ELECTRON DISTRIBUTION IN MOLECULES. II. PROTON AND FLUORINE MAGNETIC RESONANCE SHIFTS IN THE HALOMETHANES<sup>1</sup>

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Experimental chemical shifts in the proton and fluorine magnetic resonances are reported for the simple halomethanes and the chlorofluoromethanes. An analysis of the shifts and their relation to other electron-dependent parameters, such as bond distance and chlorine quadrupole coupling, demonstrates qualitatively the importance of both ionic and double-bonded electron distributions in these compounds. The electron distributions in the halomethanes are related to the electronic effects of the halogens as substituents in benzene. The proton and fluorine resonances in the fluoromethanes were multiplets, the structure arising from indirect coupling of the nuclear spins by the valence electrons. Fluorine chemical shifts were measured in a number of substituted fluorobenzenes, including the *o*-, *m*- and *p*-benzaldehydes, benzyl and benzal chlorides; the corresponding Hammett  $\sigma$ -values, estimated from the chemical shifts, are given.

### Introduction

The basic aspects of nuclear magnetic resonance absorption have been reviewed in some preceding papers.<sup>3</sup> The principle underlying the present research is that the magnetic field at a nucleus is in general not the same as that in the bulk sample, the difference arising from interactions between the applied field and the motions of the electrons in the sample.<sup>4</sup> Explicitly,  $H_0 = H_b(1 - \chi_s)$ , where  $H_0$  is the field at the nucleus;  $H_b$ , that in the bulk sample; and  $H_b\chi_s$  is an internal diamagnetism, or a nuclear magnetic shielding field. Differences in electronic environment cause easily measurable differences in  $\chi_s$  for a magnetic nucleus in different substances or even in structurally non-equivalent positions in the same molecule.

These differences are often called "chemical shifts" because they reflect the chemical state of the system. They are measured conveniently at a fixed resonance frequency as  $\delta = 10^6 \times (H_r - H_0)/H_r$ , where  $H_r$  is the applied magnetic field for the given nuclear resonance in some parent, refer-

ence compound, and  $H_0$  is the resonance field for the compound in question. Thus  $\delta$  is a quantitative measure of the differences in the electron distribution about the nuclei in the two compounds. But, unfortunately, the complexity of the effect restricts theoretical calculations<sup>4</sup> and the interpretation of experimental data is in terms of simplified, qualitative concepts.

In the first paper<sup>5</sup> of this series it was shown that chemical shifts in the magnetic shielding of fluorine nuclei in substituted fluorobenzenes could be used to analyze the effects of the substituents upon the electron distribution in the benzene ring. In this article, similar data are reported for the fluorine and proton resonances in many of the halogen substituted methanes. Multiplet resonance lines of the type described elsewhere<sup>6</sup> were observed in the fluoromethanes. In addition, some further chemical shifts data are given for the fluorine resonances in substituted fluorobenzenes.

### Experimental

**Apparatus and Procedure.**—In these experiments, the apparatus and procedure were somewhat different from the previous work.<sup>5</sup> A detailed description of the changes is

(1) Supported in part by ONR.

(2) AEC Predoctoral Fellow.

(3) Some earlier reviews have been given under the title "Nuclear Moments" in "Annual Reviews of Nuclear Science," Annual Reviews, Inc., Stanford, Calif., N. F. Ramsey, Vol. 1, 1952, p. 97; B. T. Feld, Vol. 2, 1953, p. 239. See also G. E. Pake, *Am. J. Phys.*, **18**, 438, 473 (1950).

(4) N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950); *ibid.*, **86**, 243 (1952).

(5) H. S. Gutowsky, D. W. McCall, B. R. McGarvey and L. H. Meyer, *J. Am. Chem. Soc.*, **74**, 4809 (1952). Prior work is cited there in detail.

(6) H. S. Gutowsky, D. W. McCall and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953).



being published.<sup>7</sup> Improved resolution, which was essential for measuring the proton shifts, was obtained mainly by using smaller samples. The magnetic field was that of a permanent magnet of about 4180 gauss. In the experiments, a direct observation is made of the difference required in the applied magnetic field for the resonance, at fixed frequency, in the compound and in some reference. For ease of comparison, a different reference was chosen within each class of compound investigated. Each of these class references has been established on a general scale with an arbitrarily chosen primary reference, trifluoroacetic acid for fluorine and distilled water for the proton. All measurements were made on samples in the liquid state, usually at room temperature except for low boiling gases which were condensed in a simple cryostat.<sup>7</sup> Solids were dissolved in solvents of similar chemical constitution.

**Materials.**—Highly purified samples are not required for this type of measurement; the only critical factor is that there be no question about the identity of the constituent giving the measured resonance line. In most cases, commercial materials were used, without purification. The fluorobenzaldehydes, benzyl chlorides, and benzal chlorides were purchased from Custom Chemical Laboratories; the methyl fluoride from Beta Research Laboratory, Chicago, Illinois; the methyl chloride from Ohio Chemical and Surgical Equipment Co.; and the methyl bromide and methane from The Matheson Company, Inc. The methylene chloride, bromide and iodide, the bromoform and methyl iodide were purchased from Eastman Kodak Company; the chloroform from Merck and Company; and the iodoform from Mallinckrodt Chemical Works. The remainder of the compounds were donated by the Jackson Laboratory, E. I. du Pont de Nemours and Company.

## Results and Discussion

**A. Substituted Benzene Derivatives.**—In Table I there are listed fluorine  $\delta$ -values for a number of substituted fluorobenzenes, referred to fluorobenzene.<sup>8</sup> In the previous research,<sup>5</sup> a comparison of the observed  $\delta$ -values with the corresponding Hammett<sup>9</sup>  $\sigma$ -constants for about thirty other substituents gave separate linear least squares relations for meta and for para substituents<sup>10</sup>:  $\sigma_m = 1.69 \delta_m$  and  $\sigma_p = 0.560 \delta_p + 0.271$ . It was concluded that the separate curves are a direct demonstration of the different character of the principal mechanism by which substituents affect the electron distribution at the meta and at the para positions. The rela-

TABLE I  
 $\delta$ -VALUES AND PREDICTED  $\sigma$ -VALUES FOR MONOSUBSTITUTED BENZENE DERIVATIVES

Substituent	$\delta_F$	$\sigma_{pred}$	Substituent <sup>a</sup>	$\delta_F$	$\sigma_{pred}$
<i>o</i> -CHO	-0.96	...	<i>m</i> -NHCOCH <sub>3</sub>	+0.10	+0.17
<i>m</i> -CHO	+0.10	+0.17 <sup>b</sup>	<i>p</i> -NHCOCH <sub>3</sub>	-0.57	-0.05
<i>p</i> -CHO	+0.98	+0.82 <sup>b</sup>	<i>p</i> -SO <sub>2</sub> Cl	+1.26	+0.98
<i>o</i> -CH <sub>2</sub> Cl	-0.54	...	<i>p</i> -CCl <sub>3</sub>	+0.26	+0.42
<i>m</i> -CH <sub>2</sub> Cl	+0.02	+0.03	<i>m</i> -O-C <sub>6</sub> H <sub>4</sub> -F( <i>p</i> )	-0.05	-0.08
<i>p</i> -CH <sub>2</sub> Cl	-0.07	+0.23	<i>p</i> -O-C <sub>6</sub> H <sub>4</sub> -F( <i>p</i> )	-0.67	-0.10
<i>o</i> -CHCl <sub>2</sub>	-0.51	...	<i>p</i> -NH-C <sub>6</sub> H <sub>4</sub>	-0.94	-0.26
<i>m</i> -CHCl <sub>2</sub>	+0.14	+0.24	<i>m</i> -CH(OH)CH <sub>3</sub>	0.00	0.00
<i>p</i> -CHCl <sub>2</sub>	+0.25	+0.41			

<sup>a</sup>  $\delta$ -values in this column are taken from ref. 5. <sup>b</sup> In ref. 7, p. 188, experimental  $\sigma$ -values of +0.381 and +1.126, respectively, are reported for *m*- and *p*-CHO. The poor agreement with the predicted  $\sigma$ -values is typical of +E substituents.

(7) H. S. Gutowsky, L. H. Meyer and R. C. McClure, *Rev. Sci. Instruments*, **24**, in press (1953).

(8) Fluorobenzene has a  $\delta_F$ -value of -3.56 referred to trifluoroacetic acid.

(9) L. P. Hammett, "Physical Organic Chemistry," 1st Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

(10) The  $\sigma$ -values are not defined ordinarily for ortho substituents because steric as well as electronic factors can affect reaction rates at the ortho position.

tions themselves are of use in predicting  $\sigma$ -values from  $\delta$ -values and thereby estimating the effect of the substituent on chemical reactivity, *via* the Hammett  $\sigma\rho$  method.<sup>9</sup>

The prediction of  $\sigma$  from  $\delta$  is an attractive procedure since a  $\delta$ -value can be obtained in less than a half hour with an operating high resolution spectrometer, while the evaluation of  $\sigma$  by the usual kinetic or equilibrium study is a much longer process. So,  $\sigma$ -values have been computed from the  $\delta$ -values for substituents for which no direct  $\sigma$ -values are available. These include several of the substituents examined earlier<sup>5</sup> as well as most of those reported now. The  $\sigma$ -values predicted are included in Table I.

Some of the  $\delta$ -values in Table I are particularly interesting. From chemical evidence, the aldehyde group, CHO, is classed usually as a +E substituent in the effects ascribed to the resonance or electro-meric mechanism. Previously,<sup>5</sup> an intercomparison of the *o*-, *m*- and *p*  $\delta$ -values of different substituents confirmed their division into +E and -E classes. A similar comparison of the  $\delta$ -values for CHO places it in the +E class, which includes those substituents with  $\pi$ -electrons on the atom attached to the benzene ring. The  $\delta$ -values for CH<sub>2</sub>Cl and CHCl<sub>2</sub> and those reported before for CH<sub>3</sub> and CCl<sub>3</sub> show an interesting intermediate character going toward +E in the sequence CH<sub>3</sub>, . . . , CCl<sub>3</sub>. This seems reasonable since the greater electronegativity of Cl compared to H would make electron distributions of the form  $^+\phi=C=Cl_3^-$  more stable than  $^+\phi=C=H_3^-$ .

**B. Halogen Substituted Methanes.**—In Table II there are listed the  $\delta_H$  and  $\delta_F$ -values for the simple halomethanes, and also the  $\delta_F$ -values for the chlorofluoromethanes. The proton  $\delta$ -values are given with respect to methane and the fluorine with respect to carbon tetrafluoride.<sup>11</sup> The proton and fluorine resonances in the fluoromethanes exhibited a fine structure of the electron nuclear-spin-coupling type<sup>6</sup>; these results are given and discussed in the second section following. Also included in Table II are the chlorine quadrupole coupling constants<sup>12</sup> of the chloromethanes and chlorofluoromethanes, and the available more precisely known C-H and C-F bond distances in the various halomethanes. All of these parameters have magnitudes determined in one way or another by the electron distribution in the molecule. Interrelations are to be expected, therefore, and comparisons of the various parameters in homologous series should be valuable in assessing the nature of the corresponding changes in electron distribution.

**Proton and Fluorine Chemical Shifts.**—Figure 1 presents graphically the dependence of the  $\delta_H$ -values upon the extent of halogenation in the halomethanes; and Fig. 2, that of  $\delta_F$  in the fluoro- and chlorofluoromethanes. In Fig. 1 it is seen that  $\delta_H$  increases quite uniformly in the series CH<sub>4</sub>, CH<sub>3</sub>X, CH<sub>2</sub>X<sub>2</sub> and CHX<sub>3</sub> for each of the halogens F,

(11) Methane has a  $\delta_H$ -value of -0.94 referred to distilled water, and carbon tetrafluoride a  $\delta_F$ -value of +1.24 referred to trifluoroacetic acid.

(12) A review of quadrupole spectroscopy and discussions of current work were given at the symposium by B. P. Dailey, *THIS JOURNAL*, **87**, 490 (1953), and in the two papers following it.

TABLE II  
 $\delta$ -VALUES FOR HYDROGEN AND FLUORINE IN HALOMETHANES

Compound	$\delta_H$	$\delta_F$	$d_{C-H}$ , Å.	$d_{C-F}$ , Å.
CH <sub>4</sub>	0.00	...		
CH <sub>3</sub> F	+0.71	-21.00	1.109 <sup>d</sup>	1.385 <sup>d</sup>
CH <sub>2</sub> F <sub>2</sub>	+0.88	-8.09 <sup>b</sup>	1.092 <sup>a</sup>	1.358 <sup>a</sup>
CHF <sub>3</sub>	+1.03	-1.82 <sup>b</sup>	1.098 <sup>a</sup>	1.332 <sup>a</sup>
CF <sub>4</sub>	...	0.00 <sup>b</sup>		1.322 <sup>a</sup>
CH <sub>2</sub> Cl	+0.71	62.8.40	1.109 <sup>b</sup>	
CH <sub>2</sub> Cl <sub>2</sub>	+0.99	72.2.47	1.068 <sup>c</sup>	
CHCl <sub>3</sub>	+1.18	76.6.98	1.073 <sup>c</sup>	
CCl <sub>4</sub>	...	82.1.85		
CH <sub>2</sub> Br	+0.73		1.104 <sup>a</sup>	
CH <sub>2</sub> Br <sub>2</sub>	+1.01			
CHBr <sub>3</sub>	+1.24		1.068 <sup>c</sup>	
CHI <sub>3</sub>	+0.76		1.100 <sup>a</sup>	
CH <sub>3</sub> I	+0.99			
CHI <sub>3</sub> <sup>a</sup>	+0.65			
CF <sub>3</sub> Cl	+3.68	77.7.58		1.323 <sup>k</sup>
CF <sub>2</sub> Cl <sub>2</sub>	+6.04	77.8.16		
CFCl <sub>3</sub>	+7.67	77.9.63		

<sup>a</sup> In CCl<sub>4</sub> solution. <sup>b</sup> Approximate values for these compounds were reported by H. S. Gutowsky and C. J. Hoffman, *Phys. Rev.*, **80**, 110 (1950). <sup>c</sup> R. Livingston, *This Journal*, **57**, 496 (1953). <sup>d</sup> O. R. Gilliam, H. D. Edwards and W. Gordy, *Phys. Rev.*, **75**, 1014 (1949). <sup>e</sup> D. R. Lide, *J. Am. Chem. Soc.*, **74**, 3548 (1952). <sup>f</sup> S. N. Ghosh, R. Trambarulo and W. Gordy, *J. Chem. Phys.*, **20**, 605 (1952). <sup>g</sup> L. O. Brockway, private communication. This is a recent electron diffraction result; C-F distances determined in the other fluoromethanes are in good agreement with the microwave results. <sup>h</sup> W. Gordy, J. W. Simmons and A. G. Smith, *Phys. Rev.*, **74**, 243 (1948). <sup>i</sup> R. J. Meyers and W. D. Gwinn, *J. Chem. Phys.*, **20**, 1420 (1952). <sup>j</sup> Q. Williams, J. T. Cox and W. Gordy, *ibid.*, **20**, 1524 (1952). <sup>k</sup> D. K. Coles and R. H. Hughes, *Phys. Rev.*, **76**, 858 (1949).

Cl and Br, with relatively much smaller increases in  $\delta_H$  for a given type of molecule in the sequence F, Cl and Br. Of the iodides, methyl iodide is "normal"; the  $\delta_H$ -value in methylene iodide is somewhat small compared to the other methylene halides; and the iodoform  $\delta_H$ -value is even lower than that of methyl iodide. The fact that the  $\delta_H$ -values are pretty nearly the same for all halides of a given molecular type, as for example CH<sub>3</sub>X, suggests that the changes associated with halogenation are not caused in a simple manner by electronegativity differences, but the effects of the latter are balanced partially by an opposing mechanism.

Similarly complex results were found for the proton resonance shifts in the binary covalent hydrides<sup>13</sup> and for the fluorine resonance shifts in the halogen substituted fluorobenzenes.<sup>5</sup> In the hydrogen halides  $\delta_H$  increased<sup>14</sup> in the sequence HI, HBr, HCl and HF, with HI anomalously low. The bare proton has the largest  $\delta$ -value, so this trend may be ascribed to increasing ionic character of the H-X bond. But as one goes from the group 7 to the group 4 hydrides, the dependence reverses. Thus  $\delta_H$  for CH<sub>4</sub> is less than for SiH<sub>4</sub>, even though carbon is more electronegative than silicon, suggesting that bond hybridization as well as ionic

(13) H. S. Gutowsky and C. J. Hoffman, *J. Chem. Phys.*, **19**, 1259 (1951).

(14) The original data are given in terms of magnetic shielding of the proton, referred to the bare proton as the scale zero; the  $\delta$ -scale used here reverses the sign.

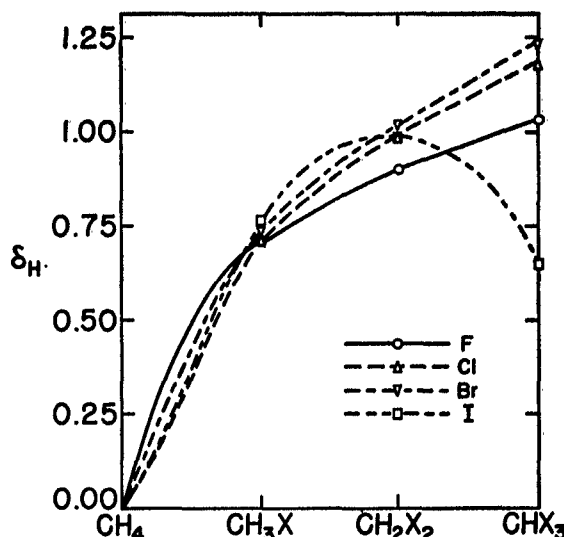


Fig. 1.—The dependence of the proton magnetic resonance shift upon extent of halogenation in the simple halomethanes.

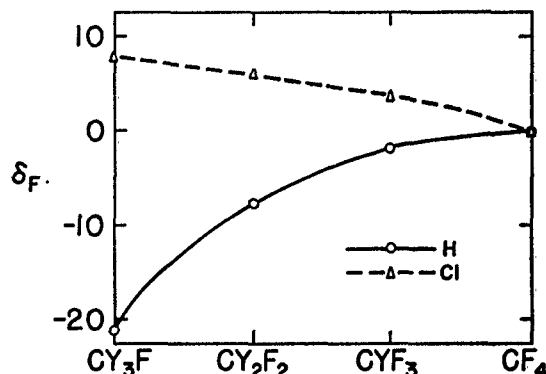
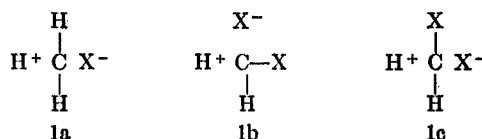


Fig. 2.—The dependence of the fluorine magnetic resonance shift upon extent of halogenation in the fluoromethanes and chlorofluoromethanes.

character may be important. However, most of the trends in  $\delta_H$  for the halomethanes in Fig. 1 can be interpreted qualitatively as changes in the ionic character of the C-H bond, though admittedly the situation is more complex.

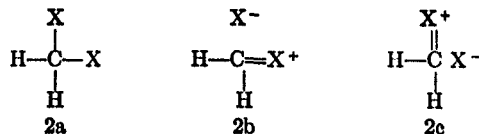
Remembering that increased ionic character increases  $\delta_H$ , the general increase in  $\delta_H$  upon successive halogenation reflects the increasing inductive effect of the halogen atoms in removing electrons from about the less electronegative protons. Or stated another way, the electron distribution in the halides incorporates larger fractions of ionic forms, as shown below, than does that in methane



Following this argument, one would expect  $\delta_H$  for a given type of molecule to follow the electronegativity order, i.e., F > Cl > Br > I. In reality, just the opposite is observed, except for methylene iodide and iodoform as mentioned above.

The substituent effects of the halides in benzene

have a similar reversal from predictions based on electronegativities alone.<sup>6</sup> The mechanism invoked there is suggested by double bonded structures of the type

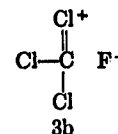
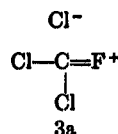


This "electromeric" or resonance effect opposes the inductive effect, making the carbon more electropositive and reducing  $\delta_{\text{H}}$ ; moreover, the order of importance is  $\text{F} > \text{Cl} > \text{Br} > \text{I}$ , as the larger atoms form multiple bonds less readily.<sup>6</sup> With the inductive and "electromeric" effects in opposition but with magnitudes depending upon the halogens in the same order, the actual sequence of resultant effect is constructed readily.

The carry-over of this relatively simple interpretation from one class of compounds to a rather different class is encouraging. However, the anomalous results for the iodomethanes emphasize the complexity of the problem. The fact that methyl iodide follows the trends of the other halomethanes while the methylene iodide and iodoform have low  $\delta_{\text{H}}$ -values suggest the difference may lie in the comparatively large size of the iodine atom. Some internal consistency prevails inasmuch as the  $\delta_{\text{H}}$ -value for HI is low compared to the other hydrogen halides.

The inductive and double-bond structures introduced in discussion of the  $\delta_{\text{H}}$ -values should apply also to the  $\delta_{\text{F}}$ -values shown in Fig. 2 for the fluoromethanes and chlorofluoromethanes. The  $\delta_{\text{F}}$ -value is small for the fluoride ion and increases quite linearly with increasing covalent character.<sup>13</sup> Formulas 1 and 2 suggest that successive fluorination of methane would introduce competition between the fluorines for the electrons from a decreasing number of hydrogens. This would reduce the ionic character of the C-F bonds and increase the  $\delta_{\text{F}}$ -values, as is indeed observed.

The double-bond mechanism is essential in explaining the continued increase of  $\delta_{\text{F}}$  on proceeding from  $\text{CF}_4$  to  $\text{CFCl}_3$  by successive substitution of chlorine for fluorine. If only inductive effects were important then, since Cl is more electronegative than H but less than F,  $\delta_{\text{F}}$  for  $\text{CFCl}_3$  should be between  $\text{CFH}_3$  and  $\text{CFF}_3$ , whereas it is found to be the largest of both series. Introducing the double-bond structures below, form 3a is more important than 3b, for chlorine forms a double bond less readily than does fluorine.<sup>6</sup>



In the simple halomethanes, the inductive effect was more important than the double-bonding; however, the electronegativity of chlorine is considerably larger than that of hydrogen, so the double-bond effect could be greater than the inductive in the chlorofluoromethanes. The net result would then be the C-F bonds becoming less ionic in the sequence  $\text{CH}_3\text{F} \dots \text{CF}_4 \dots \text{CFCl}_3$ , as shown by the observed increase in the corresponding  $\delta_{\text{F}}$ -values.

The interdependence of the C-H and C-F bond characters in the fluoromethanes is shown graphically in Fig. 3, where the  $\delta_{\text{F}}$ -values are plotted against the  $\delta_{\text{H}}$ -values for the same compound. Both  $\delta_{\text{H}}$  and  $\delta_{\text{F}}$  increase in the sequence  $\text{CH}_3\text{F}$ ,  $\text{CH}_2\text{F}_2$  and  $\text{CHF}_3$ , indicating the ionic character of the C-H bond increases as that of the C-F bond decreases. This is to be expected, for an inductive change in one part of the molecule would require balancing by an opposite effect in another part of the molecule.

**Multiplet Lines in the Fluoromethanes.**—Table III gives the structure and splittings of the multiplet proton and fluorine resonance lines in the fluoromethanes. In Fig. 4 are oscilloscope photographs of the typical proton and fluorine triplets in  $\text{CH}_2\text{F}_2$ . These multiplets arise from an indirect coupling of the fluorine and proton nuclear spins by the valence electrons; the results agree in detail with the analysis of similar multiplets in a number of inorganic phosphorus and fluorine compounds.<sup>6</sup> The coupled H and F nuclei are not directly bonded, so the magnitudes of the splittings are determined by the nature of both the C-H and C-F bonds. The spin coupling depends primarily upon the p-character of the bonds; the ionic struc-

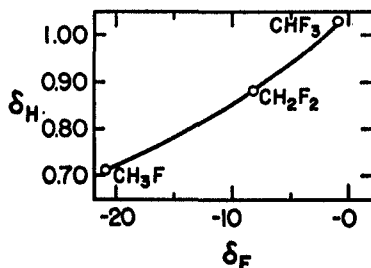


Fig. 3.—The interdependence of the proton and fluorine magnetic resonance shifts in the fluoromethanes.

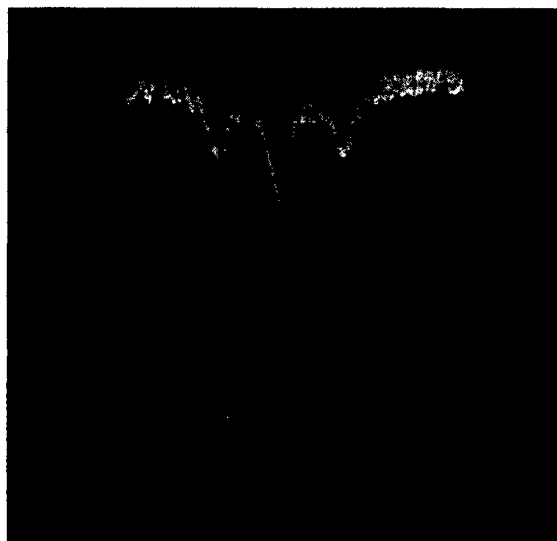


Fig. 4.—Oscilloscope photographs of the triplet proton (top) and fluorine (bottom) magnetic resonance lines in liquid  $\text{CH}_2\text{F}_2$ . The splitting of the proton line is 11.3 milligauss and that of the fluorine 13.2. The sweep amplitude is 75 milligauss for both lines.

tures and s-electrons are unimportant in this case. But since the net effect observed comes from both bonds, no conclusions can be drawn regarding either one, in spite of the systematic increase in the splitting upon successive substitution of fluorine. The results do suggest, however, that the preparation of  $C^{13}$ -concentrated halomethanes and the observation of the  $C^{13}$ -H and  $C^{13}$ -F coupling would be profitable.

TABLE III

## MULTIPLY RESONANCES IN THE FLUOROMETHANES

Compound	Proton resonance		Fluorine resonance		$H^1$ Splitting <sup>b</sup> / F <sup>19</sup> Splitting
	Structure <sup>a</sup>	Splitting, mgauss	Structure <sup>a</sup>	Splitting, mgauss	
$CH_3F$	(1-1)	9.5	(1-3-3-1)	11.0	0.865
$CH_2F_2$	(1-2-1)	11.4	(1-2-1)	13.2	0.865
$CHF_3$	(1-3-3-1)	18.4	(1-1)	20.2	0.910

<sup>a</sup> The numbers are the relative intensities of the components in each resonance. <sup>b</sup> Theoretically, this ratio should be the inverse ratio of the nuclear gyromagnetic ratios, 0.885.

**Comparisons of  $\delta_H$  and  $\delta_F$  with the Chlorine Quadrupole Coupling.**—In Fig. 5,  $\delta_H$  and  $\delta_F$  are plotted against  $|eqQ|_{AV}$  at 20°K. for  $Cl^{35}$  in the chloromethanes and chlorofluoromethanes, respectively. An increase in the p-orbital character used by the chlorine in bond formation increases the chlorine quadrupole coupling constant, while increased ionic character and double-bond character decrease the coupling.<sup>12</sup> In the chloromethanes, both  $\delta_H$  and the chlorine coupling increase upon successive chlorine substitution. This indicates the ionic character of the C-H bond increases as that of the C-Cl bond decreases, primarily an inductive effect analogous to that found in the fluoromethanes discussed above.

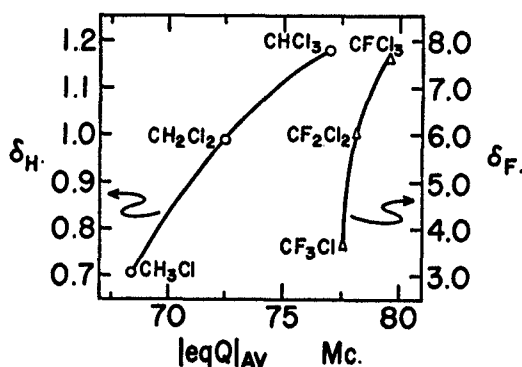


Fig. 5.—The interdependence of the magnetic resonance shifts and the chlorine quadrupole couplings in the chloromethanes and chlorofluoromethanes.

In the chlorofluoromethanes, both  $\delta_F$  and the chlorine coupling increase upon successive chlorination, suggesting in this case decreasing ionic character of both the C-F and C-Cl bonds. The double-bond structures such as 3a and 3b proposed above in explanation of the decreasing C-F ionic character also account for the decreasing C-Cl ionic character, if the same assumption is made that the double-bond effects exceed the inductive. In  $CF_3Cl$ , all three C-F bonds try to form structures  $Cl-C=F^+$ , so the single C-Cl bond has a high ionic character while the three C-F bonds have low double-bond

character. In  $CFCl_3$ , on the other hand, there is only one C-F bond feeding electrons into three chlorines, so the C-F bond has an increased double-bond character, while the C-Cl bonds have decreased ionic character, agreeing with experiment.

**$\delta_H$ ,  $\delta_F$  and the C-H and C-F Bond Distances.**—In Fig. 6  $\delta_H$  is plotted against the corresponding C-H bond distances, and in Fig. 7,  $\delta_F$  against the C-F distances. For both nuclei, increasing  $\delta$ 's are associated with decreasing bond distances. The increase in  $\delta_H$  indicates that increasing ionic character occurs with decreasing C-H bond length. This agrees with the suggestion of Schomaker and Stevenson<sup>15</sup> that ionic character reduces bond lengths. The proton data are of further interest in that the points for the  $CH_3X$ ,  $CH_2X_2$  and  $CHX_3$  molecular types fall along different curves, with the halogens in the same sequence for each type.<sup>16</sup> In the discussion, Dailey pointed out that the accuracies of the microwave analyses are limited by zero-point vibrational effects<sup>16</sup>; however, the differences between the different molecular types are large enough to be real, suggesting changes in bond

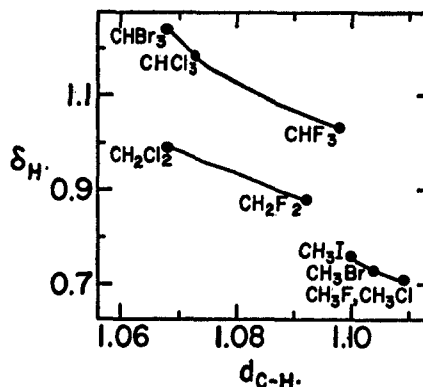


Fig. 6.—The interdependence of the proton magnetic resonance shifts and the C-H bond distances in the halomethanes.

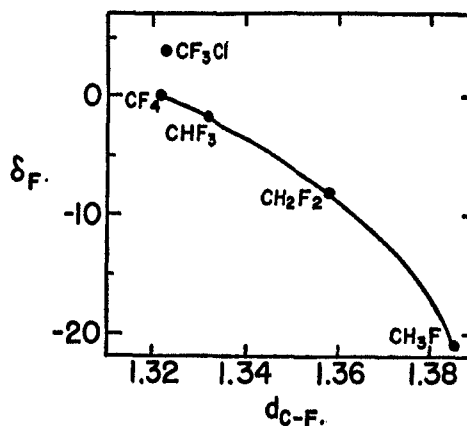


Fig. 7.—The interdependence of the fluorine magnetic resonance shifts and the C-F bond distances in the halomethanes.

(15) V. Schomaker and D. P. Stevenson, *J. Am. Chem. Soc.*, **63**, 37 (1941).

(16) The trend shown for the methyl halides is not borne out by the recent detailed analysis of the microwave data, by S. L. Miller, L. C. Aamodt, G. Doumanis, C. H. Townes and J. Kritchman, *J. Chem. Phys.*, **20**, 1112 (1952).

hybridization as well as in ionic character. On the basis of the  $\delta_H$ -values and the trends in Fig. 6, the C-H bond distances in  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{I}$  should be both about 1.065 Å., while that in  $\text{CHI}_3$  might be as large as 1.12 Å.

The  $\delta_F$ -values show *decreasing* ionic character with decreasing C-F bond length. This agrees however with the double-bond shortening proposed by Pauling<sup>17</sup> provided the double-bond structures are more important than the ionic in determining the C-F bond length. The point for  $\text{CF}_3\text{Cl}$  in Fig. 7 confirms the greater importance of the double-bond structures in the chlorofluoromethanes compared to the fluoromethanes, as suggested in an earlier section.

**C. General Comments.**—In conclusion, the most striking feature of these results is probably their internal consistency. A wide range of molecular parameters are at least qualitatively fitted by a few quite simple concepts. Some features, for instance the chemical shift data on the iodides, are not clear. But, with continued research on the various halomethanes, with observations such as the bromine and iodine quadrupole coupling constants, with additional good bond distances as well as the determination of force constants from vibrational spectra, it should prove possible to make more critical tests of our notions about

molecular structure. And, of course, it is to be hoped that quantitative as well as qualitative agreement will be reached.

**Acknowledgment.**—We wish to thank Mr. Apollo Saika for his assistance with the measurements, and the Jackson Laboratory, E. I. du Pont de Nemours and Company, for generously donating many of the samples. A Grant-in-Aid from the Research Corporation provided most of the equipment.

## DISCUSSION

**B. P. DAILEY** (Columbia University).—In attempting correlations between microwave bond-lengths and the chemical shifts, one must recognize that the bond lengths are really averaged over the vibrational state.

**B. BOLGER** (Pennsylvania State College).—When one regards chemical shifts, one has also to take into account a second order paramagnetism, which can appear when there exist several low lying states of the molecule near the ground state. As this effect is often greater than the diamagnetic shift (for several Co salts nearly 1%), has this effect been taken into account in these experiments?

**H. S. GUTOWSKY.**—The separation of the chemical shifts, by Ramsey, into a diamagnetic term and a second-order paramagnetic term is rather artificial, and was done mainly for computational purposes. The analysis given here is qualitative, and is based largely on the empirical result that the chemical shifts in the binary fluorides and hydrides can be related simply to the ionic characters of the bonds, and this is independent of what may be the actual magnitudes of the opposing diamagnetic and second order paramagnetic terms in the theoretical treatment.

(17) L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1945, p. 236.

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